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IMPROVED MECHANICAL PROPERTIES AND OZONE RESISTANCE OF RADIATION CURED SBR

August 1991

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ABSTRACT

This report is a continuation and extension of the work of the earlier Army contract, where the superiority of the electron beam cured styrene butadiene rubber (SBR) tank pads to the sulfur cured pads was demonstrated. The focus of the present study is the investigation of the extraordinary ozone resistance of our radiation cured SBR, and also on possible alternatives for SBR, butadiene rubber (BR) in particular, as a tank pad compound. Base formulations of a fully sulfur cured system were established with 5% reproducibility, and results were confirmed by mechanical properties measurements on identical formulations from Belvoir Research Development and Engineering Center (BRDEC). Constant mechanical properties as a function of exposure to ozone indicate either competitive cross-linking and scissioning reactions or a "protective" effect caused by higher terminal vinyl concentrations in the radiation cured formulations. In addition, Fourier transform infrared (FTIR) studies utilizing the horizontal attenuated total reflectance technique suggest that (1) ozone attack is correlated with lower terminal vinyl concentration and (2) there is no clear evidence of unsaturation loss by ozone addition as described in published mechanisms.

A statistical method, factorial design, was applied to develop a set of experiments to determine the effect of pertinent factors, to develop model adequacy, and to predict final mechanical properties of various SBR formulations. The ultimate objective was the establishment of the optimum concentrations which achieve the most desirable set of mechanical properties and ozone resistance values. The optimum properties were obtained for formulation partially cured with 0.5 pphr sulfur, and a post cure by an absorbed dose of 15 Mrad.

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1. INTRODUCTION

This report is a continuation and extension of the work supported by an earlier Army contract (1) Technical Report 13215 (Oct., 1986); contract DAAE07-84C-R086, where the superiority of electron beam cured tank pads was demonstrated over its sulfur cured equivalent. The present study investigates the extraordinary ozone resistance of our radiation cured SBR (Appendix-C), and also possible alternatives, butadiene rubber (BR) in particular, as tank pad compound.

2. OBJECTIVES

(1) Establishment of a data base of mechanical properties and ozone resistance of various batches of fully sulfur cured formulations.

(2) a study of BR as a possible alternative for SBR as a tank pad compound.

(3) Development of a mechanism for outstanding ozone resistance for combined sulfur-radiation cured SBR.

(4) A parametric study utilizing the statistical method, factorial design, to determine the optimum concentrations for the most desirable set of mechanical properties and ozone resistance values.

3. CONCLUSIONS

The accomplishments and conclusions derived from our study demonstrate that, to a considerable extent, our objectives were met:

- A complete setup of mixing, vulcanizing, and testing generated mechanical properties which are reproducible to within ± 5%.
- A competitive crosslinking and scission reactions, and the nature of ionizing radiation induced crosslinks, containing high concentrations of vinyl groups, are the mechanisms by which radiation cured SBR samples resist ozone attack.
- Butadiene rubber (BR) modified by our methods is a potential alternative for SBR as a tank pad compound with a remarkable hot tear strength. The addition of 0.5 pphr of sulfur in this work proved useful in reducing dose requirements for excellent mechanical properties but did not provide ozone resistance.
- Factorial design statistical analysis gave the most desirable set of mechanical properties by optimizing concentrations of three of the ingredients.

- Our ozone test procedure requires adjustment but the results reported here do not conflict with or cast doubt on the previous findings of outstanding ozone resistance by BRDEC and, more recently, by the National Institute of Standards and Technology (NIST).
- Additional factorial design information, particularly in the effect of sulfur concentration is needed for better specification of optimum formulation.

4. BACKGROUND

4.1 THE THEORY BEHIND OZONE ATTACK ON ELASTOMERS

4.1.1 ELASTOMER MORPHOLOGY

Elastomers have unique properties which are a result of specific characteristics of the long-chain macromolecules, their interactions and morphology. Vulcanization or curing is essential in order that rubber deformation be reversible. The intermolecular crosslinks that are the consequence of curing prevent the bulk slippage of the molecules past each other and eliminate flow. Crosslinks can be introduced chemically or by means of ionizing radiation. In the former the link may be a polysulfide group; in the latter, it is typically a C-C bond. When a stress is applied to a crosslinked elastomer, equilibrium is established rapidly. Stretching a chain decreases its entropy and requires a force related to the distribution of crosslinks. This leads to a relationship between the applied stress and the material elongation (2,3). For uniaxial tension, the stress σ is related to the stretch ratio λ ,by

$$\sigma = \rho R T (\lambda - 1/\lambda^2) / M_c$$

where ρ is the density , R the universal gas constant, M_c the average molecular weight of the polymer between crosslinks, and T the absolute temperature. When a material is stretched to failure, there is a local strain such that some of the extended molecular chains undergo scission. This requires that the load be redistributed among adjoining chains with increasing strain leading to further scission and eventually inducing a critical crack or failure of the sample.

4.1.2 OZONE CHEMISTRY

Because ozone induced degradation is an important practical problem, ozone has been the subject of many studies almost from the time of its discovery by Schonobein in 1840. It is produced in small atmospheric amounts by various natural and artificial sources. These include: the action of sunlight on smog components, lighting, power transmission lines and nuclear radiation. Commercially ozone is generated in large amount by the passage of dry oxygen-bearing gas or air through a corona discharge. Another method of ozone generation is by ultraviolet radiation. For practical generation of ozone by this method a low-pressure mercury lamps of about 10 W can be used. This technique is utilized in our laboratory for ozone resistance tests.

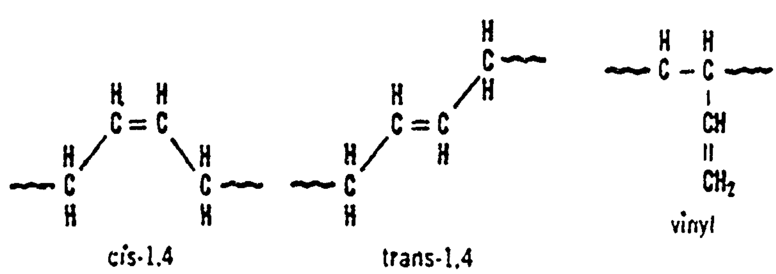
4.1.3 SIMULTANEOUS CROSSLINKING AND SCISSION

The nature and magnitude of the effects of ionizing radiation on elastomers is not as obvious as the other modes of interaction such as ozone. Mechanical consequences of ionizing radiation on elastomers are crosslinking and scission reactions. Intermolecular crosslinking is the formation of new chemical bonds between individual long chain molecules, whereas scission is the destruction of bonds in the backbone of the macromolecule. Linear polymers undergo both crosslinking and main-chain scission when subjected to ionizing radiation, with one mechanism generally dominating the other. In the case of the SBR and BR, crosslinking is dominant.

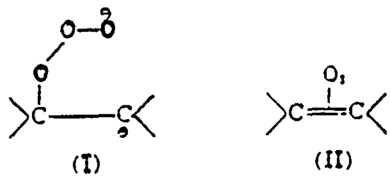
4.1.4 The Mechanism of Ozone Degradation

Of special interest in this work is ozone damage to elastomers in general and SBR in particular. There are six modes by which polymers undergo aging or degradation. They are thermal degradation, mechanical degradation, photodegradation, biodegradation, enzymatic degradation, and chemical degradation. Ozone degradation, a chemical mode of aging, involves the breaking of bonds. It can begin by an attack on side groups or atoms but the ultimate damaging effect is the scission of the C=C bonds in the main chain. Ozone reacts with many classes of organic compounds where there is a transfer of only one oxygen atom, while the other two evolve as molecular oxygen. Examples of such compounds are amines and sulfides. In other cases, there is the confusion of whether ozone or oxygen, which is present in most ozone reactions (ozonation) is the true oxidant. Only olefins and acetylenes have the ability of accepting all three oxygen atoms of the ozone molecule (5).

SBR comonomer contains butadiene units which have the three following forms:

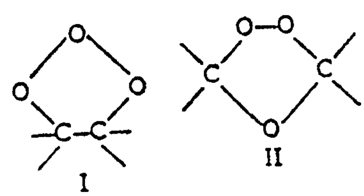


The cis-1,4 and trans-1,4 constitute 63.5%of the polymer weight, whereas the vinyl makes up 13% . In addition the styrene units which have the form CH_2=CH-C_6H_5 account for the remainder (23.5%). The butadiene olefinic double bonds are susceptible to ozone attack causing scission(6). Early investigation of ozone attack of olefins showed two possible ways: a four center process and an electrophilic one. In an electrophilic attack, a carbonium in (I) or a complex (II) can be the first intermediate:

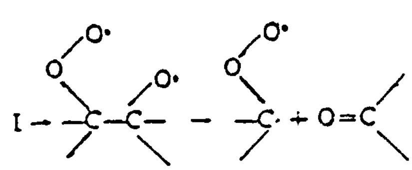


This was first proposed by Sixma et al. (7). On the other hand Nakagawa et al. (8) suggested a four-center addition of the ozone molecule to the unsaturated bond. During ozonization which precedes the formation of cracks, carbonyl and carboxyl groups are formed. At present, two acceptable mechanisms of ozone reaction with olefinic double bonds lead to the formation of carbonyl and carboxyl groups.

According to Benson (9), ozone reaction with olefinic double bonds leads to the formation of five-membered cyclic intermediates (I&II)

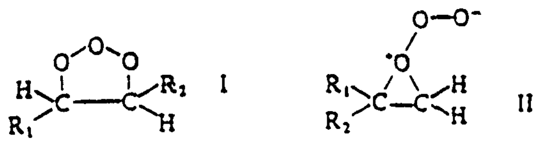


and he concluded that (I) decomposes into a carbonyl and biradical:

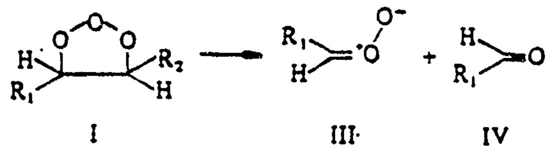


This scission reaction produces a ketone as one of its products.

Another well known mechanism is the one proposed by Criegee (10). He considers the following initial reaction:



Then, (I) decomposes to give a zwitterion (III) and a carbonyl compound (IV).



This scission reaction produces an aldehyde. Perhaps the most interesting aspect is that the reactive fragments produced by the scission reaction of either mechanisms could also lead to a crosslink.

5. DISCUSSION

5.1 REPRODUCIBLITY OF U.Md. MIXING SYSTEMS

Most of the sample preparation (i.e. mixing and vulcanizing) for our earlier contract (1) was performed at Belvoir RDEC or participating industrial facilities. An important feature of this study is the fact that all the mixing, vulcanizing, and testing was done at our laboratories, which left us in control of all the varying parameters of importance. In order to establish a standard procedure for mixing our elastomers to suit our laboratory capabilities and to produce the desired mechanical properties, we consulted with Brabender Instruments Inc. (10) which supplied our internal mixer. Standard mixing procedures for both SBR and BR were established and are presented in Appendix-A.

Six batches of fully sulfur cured formulations were prepared, four of which followed a procedure where the mixing cycle is not interrupted. All mechanical property test results are shown to be reproducible to ± 5% . Mechanical properties and hot tear measurements correspond to ASTM D412 Die-C and D624 Die-C respectively. Two modified mixing procedures were utilized leading to changes of 15% in mechanical properties. Data from BRDEC and industrial participants confirmed our results within ± 10% (11), (see Appendix-B). The mechanical properties are listed in table 5-1. The ozone resistance results are inconsistent with the previously reported data, in the sense that over 50% of the exposed samples survived the accelerated ozone test. Similar results were obtained from samples prepared by BRDEC laboratory, assuring the validity of our mixing procedure. In addition, we have an independent method of ozone concentration measurements inside our OREC ozone chamber. A simulation of our testing conditions (i.e. ozone concentration of 4 ppm, temperature of 40 °C) were performed by BRDEC group and the results are in contradiction to our data

TABLE 5-1

MECHANICAL PROPERTIES OF SBR FORMULATIONS FOR FULLY SULFUR CURED SYSTEMS PREPARED AT U.Md.

Batch No. (26NM)	Tensile Strength (Psi)	200% Modulus (Psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
1	3949±144	902±42	511±9	137±17
2	3889±202	1041±100	482±12	114±14
3	3738±291	1121±88	475±38	118±10
4	3724±155	1090±17	473±14	105±10
5	3960±180	1010±33	493±23	113±13
6	3424±200	946±16	452±19	116±9
Standard Deviation: (Among Batches)	±195	±88	±20	±13
BRD&EC:				
SBR-26A	3730±430	1170±62	430±3	
SBR-26B	4160±275	1180±103	450±26	
Colonial:				
Col2	3659±221	1185±63	405±23	

NOTE:

a. Batch no. 1 used the second approach (see mix. procedure)
b. Batches no's. 2-5 used the first approach (see mixing procedure)
c. Batch no. 6 used the second approach with the exception that sulfur and santocure were added in the roll mill.
d. SBR-26A contains U.Md. mixing ingredients and BRDEC base rubber.
e. SBR-26B contains BRDEC mixing ingredients and U.Md. base rubber.

* Hot tear tests were performed at 250 °F in correspondence with ASTM D624-Die C.

TABLE 5-2

OZONE RESISTANCE TEST FOR SBR FORMULATIONS FOR FULLY SULFUR CURED SYSTEMS AT U.Md.

Batch No. (26NM)**	No. of Samples	No. of Failures	Ozone Resistance* (Days) Failure	Ozone Resistance* (Days) Survival
1	6	2	1,46	115
2	6	3	4,36,46	115
3	6	3	.083,64 ,64	115
4	6	2	21(2)	115
5	6	3	.08,5,34	115
6	6	0		83
26-1	6	2	0.08	121
26-2	6	2	0.12	119
26-40	6	1	0.75	51
SBR-26A	2	1	0.08	>10
SBR-26B	2	0		>10

*: AS of 6-7-1990
All samples were removed on 6-7-1990 to allow space for new samples.
**: Formulations for all tested samples are listed in table 5-6.
Ozone Resistance tests are in correspondence with ASTM D1149.

since, all samples tested failed within 6 hours of ozone exposures at the same testing conditions. Samples failure refers to the time at which the first appearance of cracks on the surface is observed. Resolution of this contradiction is one of the objectives of our future work. This unresolved question does not cast doubt on the superior resistance of the radiation crosslinked specimens first reported by BRDEC, and confirmed and extended in this study at NIST ozone chamber by R. Stiller and M. Al-Sheikhly. The ozone resistance data obtained in our ozone chamber are presented in table 5-2. The explanation of this behavior is yet to be unraveled.

A comparison study for various combinations of sulfur and santocure was conducted and the results are presented in table 5-3. A formulation which contains 1.5 pphr sulfur and 1.5 pphr santocure with the rest of the mixing ingredients remaining the same, gave the most desired mechanical properties. It was selected to be the base formulation for all further research with fully sulfur cured formulations.

The attention later was devoted to reproduce our earlier SBR partial sulfur-radiation cured mechanical properties. When the sulfur precure was followed by a gamma post curing the mechanical properties, except for modulus, matched results of the similar experiments of our previous work within 10%. The discrepancy with respect to modulus is not understood (1,12). The

TABLE 5-3

COMPARISON OF MECHANICAL PROPERTIES OF SBR FOR VARIOUS COMBINATIONS OF SULFUR AND SANTOCURE

Sulfur C. (pphr)	Santocure C. (pphr)	Tensile S. (psi)	200% M. (psi)	Elong. (%)	Hot Tear (lb/in)
2.0 (26NM)	1.5	3781±195 (6 Batches)	1018±38	481±20	117±13
1.5 (26-1)	**1.5**	**4093±102**	**759±72**	**591±30**	**176±22**
1.5 (26-2)	2.0	3951±125	833±52	553±15	140±9
1.5* (26-40)	1.5	3879±113	593±37	620±14	200±23

NOTE: A minimum of 3 samples per data point were tested.

* The content of carbon black is 40pphr.

The mixing of all formulations followed the second approach.(see appendix-A).

TABLE 5-4

MECHANICAL PROPERTIES OF SBR FORMULATIONS FOR PARTIALLY SULFUR CURED SYSTEMS

Formulation Code*	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
26-3/0	1029±27	238±8	839±14	69±2
		(GAMMA IRRADIATION)		
26-3/10	2798±86	643±30	696±21	155±17
26-3/15	3161±170	691±15	647±17	204±22
26-3/20	3237±319	1114±27	555±43	139±16
		(ELECTRON BEAM)		
26-3/10	2604±286	743±14	702±7	220±7
26-3/15	3215±188	783±18	648±24	234±4
26-3/20	3474±92	1060±198	577±72	232±9
BRDEC (earlier contract):				
		(GAMMA IRRADIATION)		
26-3/10	3070	500	665	180±5
26-3/15	3395	655	610	182±6
26-3/20	3580	780	570	146±24

Note:

* Formulation 26-3 is given in table 5-6; the number after the slash is the dose in Mrad.

TABLE 5-5

OZONE RESISTANCE FOR PARTIALLY SULFUR CURED SBR FORMULATIONS

Formulation Code	No. of Samples	No. of Failures	Ozone Resistance* (Days) Failure	Survival
26-3	6	0		30
		(GAMMA IRRADIATION)		
26-3/10	6	2	0.04	30
26-3/15	"	0		43
26-3/20	"	3	0.04	30
		(ELECTRON BEAM)		
26-3/10	6	0		>30
26-3/15	"	"		>30
26-3/20	"	"		>30

Note:

* As of 2-13-91

O_3 Concentration of ozone in the chamber is 4 ppm [400 mPa].

Maximum allowed O_3 exposure is 30 Days.

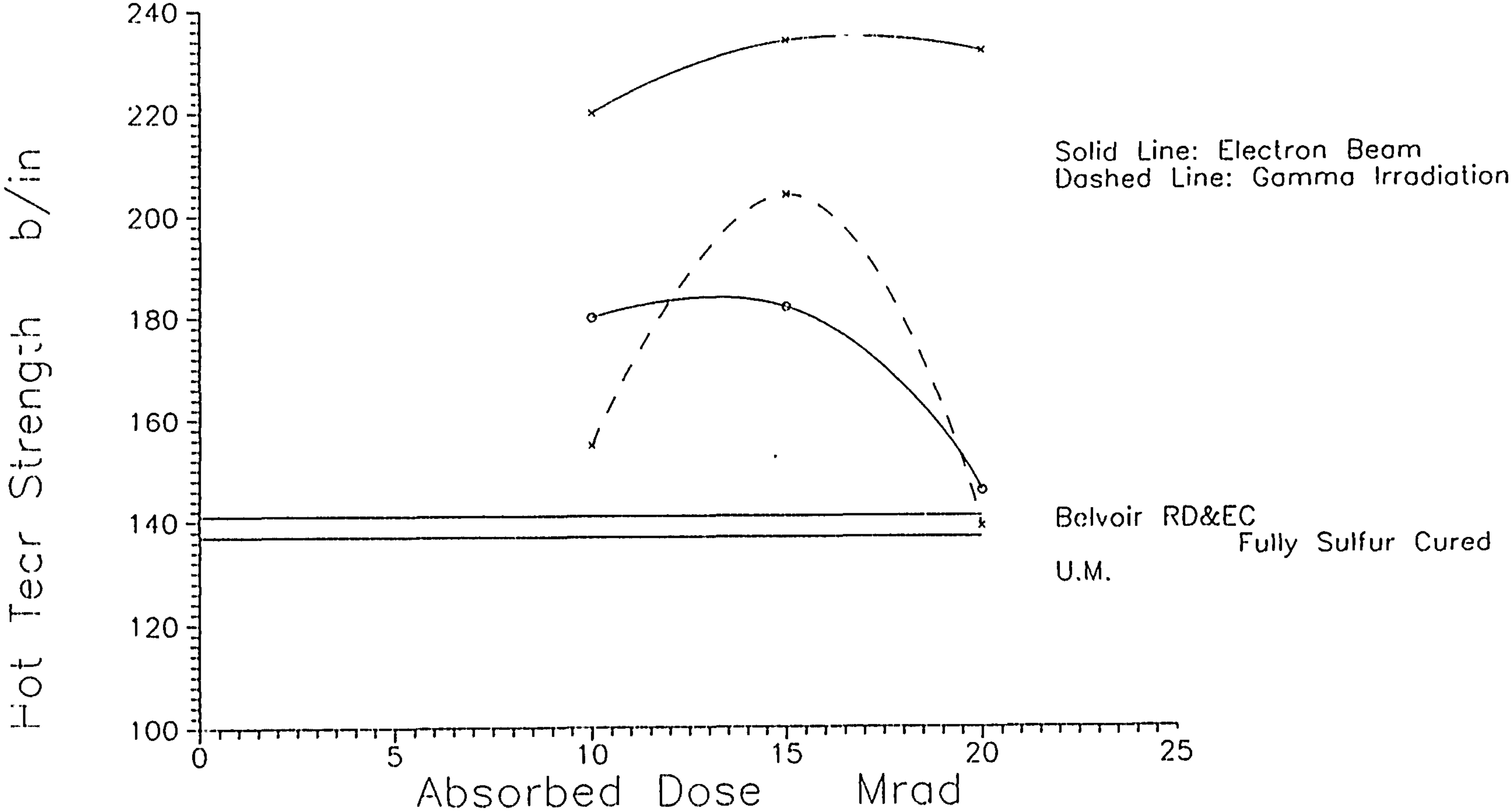


Fig.1 Hot tear strength vs. absorbed dose for partially sulfur cured SBR: (x) U.M. samples , (o) BRDEC from earlier contract

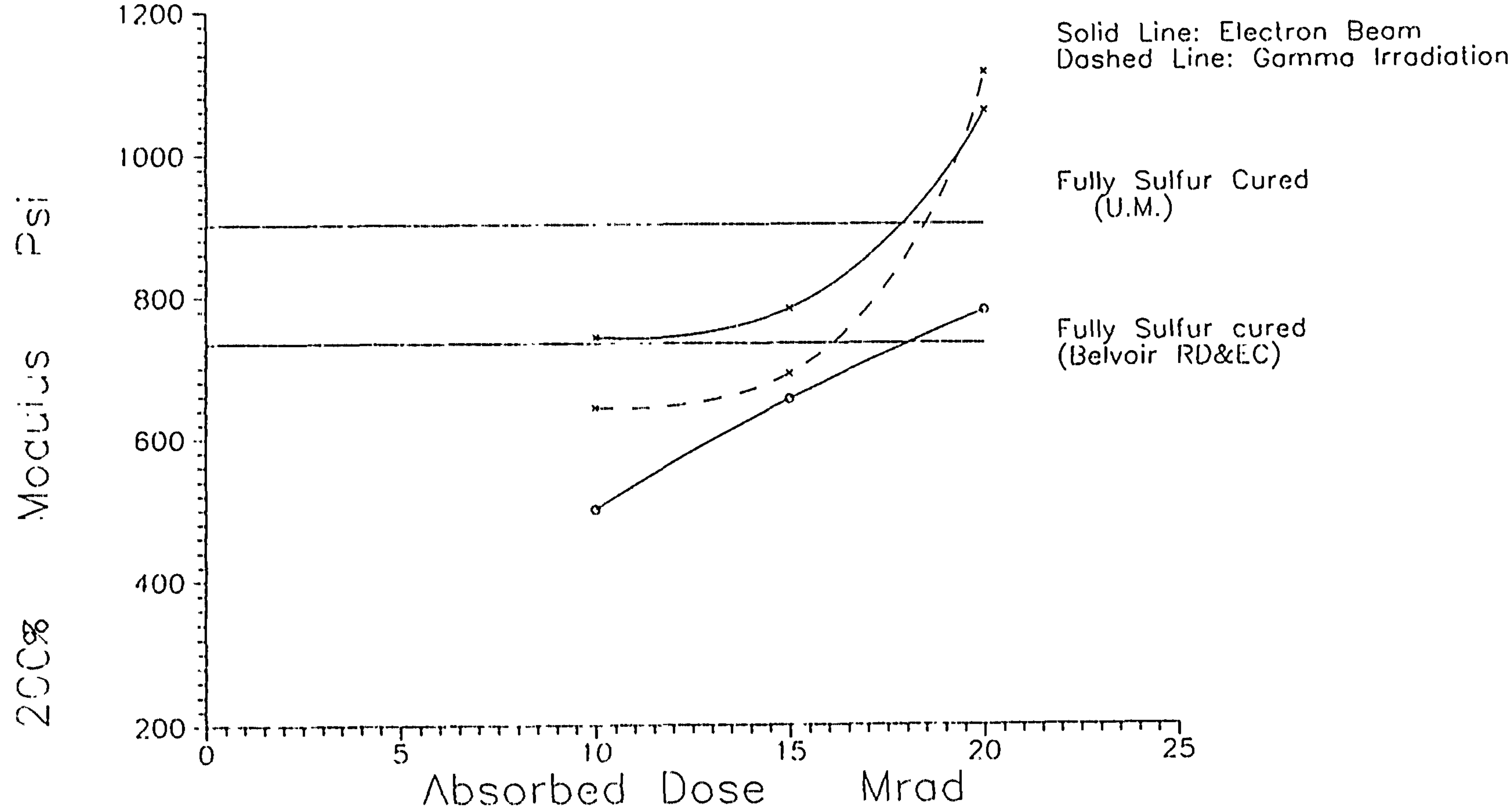


Fig.2 200 % Modulus vs. absorbed dose for partially sufur cured SBR:
(x) U.M. samples , (o) BRDEC from earlier contract.

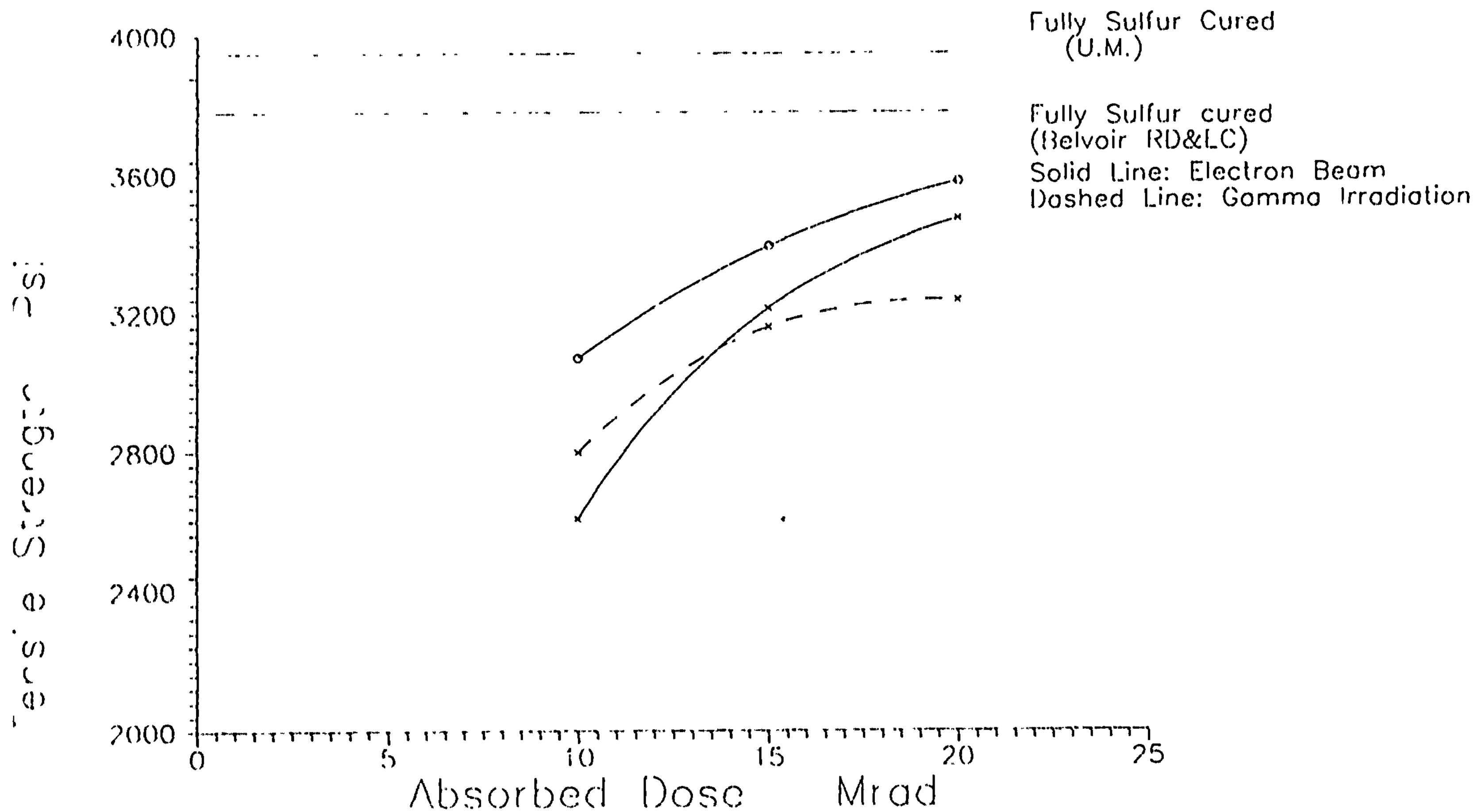


Fig.3 Tensile Str. vs. absorbed dose for partially sufur cured SBR: (x) U.M. samples , (o) BRDEC earlier contract.

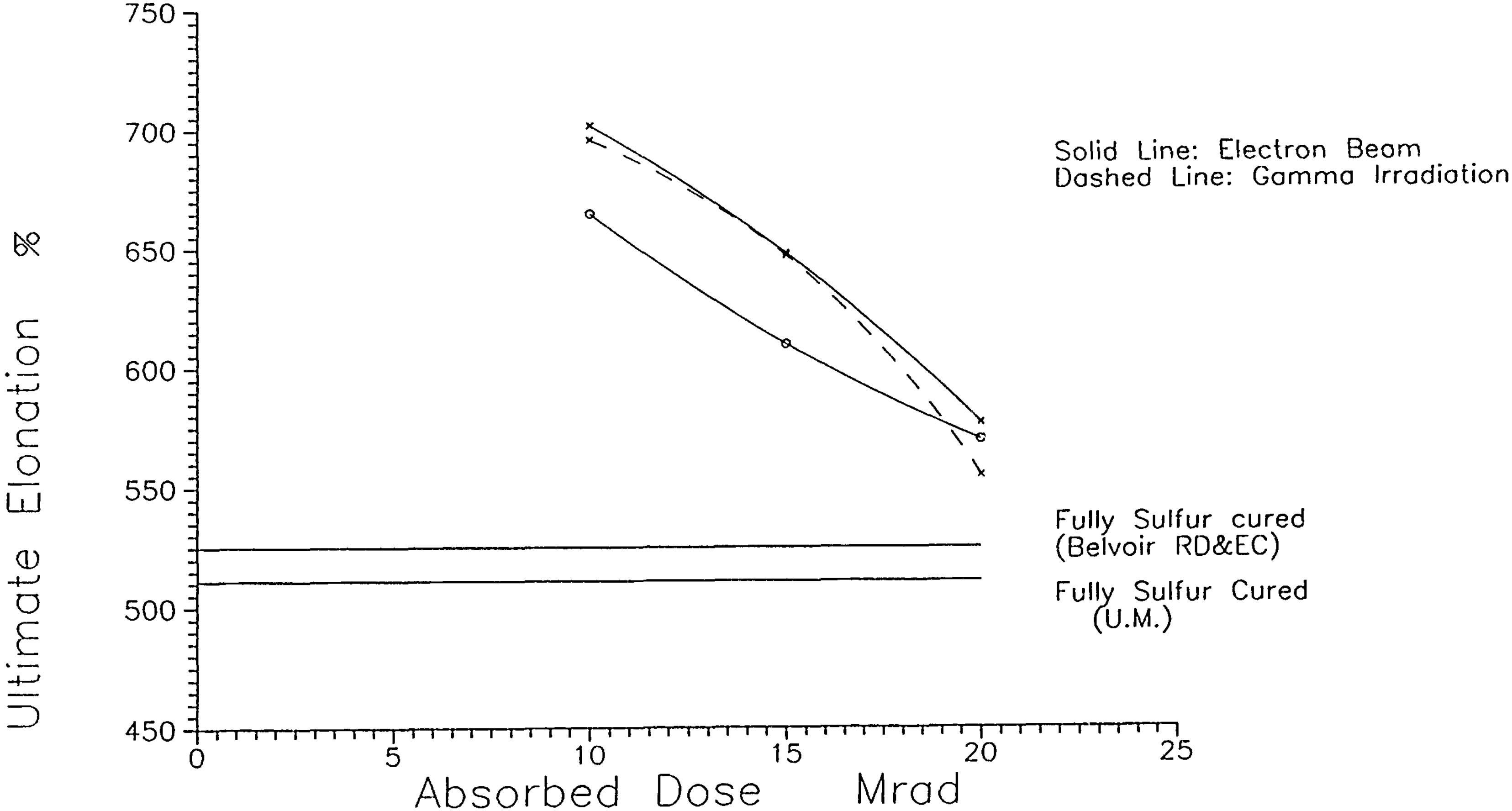


Fig.4 Ultimate Elog.vs. absorbed dose for partially sufur cured SBR: (x) U.M. samples, (o) BRDEC from earlier contract.

TABLE 5-4[T]

MECHANICAL PROPERTIES OF SBR FORMULATIONS FOR PARTIALLY SULFUR CURED SYSTEMS

Formulation Code*	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
{ GAMMA IRRADIATION }				
26-3/10[T]	2817±21	647±46	712±9	179±29
26-3/15[T]	3286±132	763±24	662±18	163±19
26-3/20[T]	3619±46	924±80	582±62	242±14
{ ELECTRON BEAM }				
26-3/10[T]	2853±249	733±67	628±33	202±3
26-3/15[T]	3187±73	654±32	761±57	232±24
26-3/20[T]	3326±159	577±33	1019±53	249±6

Note: * Formulations are listed in table 5-6; the number after the slash is the dose in Mrad.

T Formulations containing 0.1 pphr crosslinking agent (DTUD).

TABLE 5-5[T]

OZONE RESISTANCE FOR SBR FORMULATIONS

Formulation Code	No. of Samples	No. of Failures	Ozone Resistance* (Days) Failure	Survival
{ GAMMA IRRADIATION }				
26-3/10[T]	6	0		30
26-3/15[T]	"	1	0.04	30
26-3/20[T]	"	2	0.04	30
{ ELECTRON BEAM }				
26-3/10[T]	6	0		30
26-3/15[T]	"	"		30
26-3/20[T]	"	"		30

Note:

* As of 2-20-91

O_3 Concentration of ozone in the chamber is 4 ppm [400 mPa].

Maximum allowed O_3 exposure is 30 Days.

TABLE 5-6

SBR FORMULATIONS PREPARED AT U.Md.
MIXING LABORATORY

Nomenclature	Ingredients (pphr)				
15 SBR	COPO	N110 Carbon black	[a]Additives	Santocure	Sulfur
26NM	100	45	10.5	1.5	2.0
26-1	"	"	"	1.5	1.5
26-2	"	"	"	2.0	1.5
26-40	"	40	"	1.5	1.5
26-3	"	45	"	1.5	0.5

Note:

a:

Additives	pphr
Zinc-Oxide	4.0
Stearic Acid	2.0
Antiozonant (Antiozite 2)	3.0
Antioxidant (Agerite White)	0.5
Antioxidant (Agerite Resin D)	1.0
	10.5

ozone resistance was also excellent as before. The mechanical properties and ozone resistance data are presented in tables 5-4 and 5-5, and figs 1-4. Electron beam post-curing using 2.8 Mev electrons at Irradiation Industries, Inc. (I^3) facility produced mechanical properties which are superior to their gamma ray cured counterparts. The ozone resistance of these formulations was shown to be remarkable. (See table 5-5). The formulations for both partially and fully sulfur cured SBR are presented in table 5-6. Formulations with and without the crosslinking agent (DTUD) which was incorporated in the previous work (1), were investigated to identify any advantages of the agent. The mechanical properties and ozone resistance test results for partially sulfur-radiation cured formulations with the agent are presented in table $5\text{-}4^T$ and $5\text{-}5^T$. The mechanical properties of both formulations did not demonstrate any significant differences over the dose variation. Similarly the ozone resistance was excellent in both cases. These observations demonstrate that the crosslinking agent (DTUD) is, if anything a negative influence on the dose requirements in radiation cured SBR systems when partial precuring with sulfur is performed. This is in conflict with data from previous work (1) performed on sulfur free samples mixed at BRDEC; DTUD at 0.1 pphr provided small advantages at doses up to 25 Mrad.

Industrial participants namely, Colonial Rubber (Col) and Industrial Rubber Company (IRC), supplied us upon request with a set of partially and fully sulfur cured formulations. This segment of our work focused on establishing a minimum content of sulfur and absorbed dose for partially sulfur cured SBR, in order to achieve full cure conditions. A range of SBR formulations containing sulfur contents from 0.1 - 0.5 pphr were supplied by Colonial Rubber, and were tested for mechanical properties and ozone resistance. The results of both tests are demonstrated in tables 5-7 and 5-8. Note that all Col samples failed the ozone test (table 5-8) for reasons unknown to us. Because of the unexpected nature of the results, the hot tear strength measurements were not done. These data can not be the basis of establishing a lower limit of sulfur content; this to be the subject of further investigation. Results on SBR with 1 pphr of sulfur obtained with a different mixing procedure indicate a drop of 5 Mrad in the dose requirements to achieve both enhanced static mechanical properties and excellent ozone resistance. These are tentative and are to be checked using the standard procedure. Also, a partial sulfur SBR formulations containing 0.5 pphr sulfur were supplied by IRC, and the same tests were performed (see previously mentioned tables). Our assessment is that a minimum concentration of 0.5 pphr of sulfur is required to utilize radiation curing techniques of both gamma ray and electron beam; with lower sulfur content, it is clear that much higher doses are required to achieve acceptable properties. The formulations of all samples used in this study are listed in table 5-9.

TABLE 5-7

MECHANICAL PROPERTIES OF SBR FORMULATIONS
PREPARED BY INDUSTRIAL PARTICIPANTS

Formulation Code**	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
Col2	3659±221	1185±63	405±23	--
Col.1	611±16	149±4	956±16	--
Col.1/20	3714±134	713±14	512±70	--
Col.1/30	3501±87	1070±46	447±5	--
Col.1/40	2644±449	1689±55	276±38	--
Col.2	102±4	96±3	999±39	--
Col.3	1085±36	178±5	832±75	--
Col.4	1240±82	179±15	901±34	--
Col.5	1950±154	232±13	979±118	--
Col.5/20	3794±67	999±2	467±5	--
Col.5/30	3154±212	1406±114	353±5	--
Col.5/40	2840±211	1928±80	270±17	--
Gamma:				
IRC.5	1462±19	255±20	799±21	121±15
IRC.5/20	3368±104	662±43	573±19	198±16
IRC.5/30	3354±71	977±40	497±12	*
IRC.5/40	3168±88	1150±48	432±9	*
Electron Beam:				
IRC.5/20	3302±176	597±24	613±28	227±25
IRC.5/30	3106±135	825±34	521±13	130±25
IRC.5/40	3138±127	973±60	474±19	108±11

Note: * No samples available for this test.
** Formulations are listed in table 5-9; the number after the slash is the dose in Mrad.

TABLE 5-8

OZONE RESISTANCE TEST FOR SAMPLES PREPARED BY INDUSTRIAL PARTICIPANTS

Formulation Code	No. Of Samples	No. Of Failures	Ozone Resistance* (Days) Failure	Survival
Col2	6	6	0.02	
Col.1/20	"	"	"	
Col.1/30	"	"	"	
Col.1/40	"	"	"	
Col.2/20	"	"	"	
Col.2/30	"	"	"	
Col.2/40	"	"	"	
Col.3/20	"	"	"	
Col.3/30	"	"	"	
Col.3/40	"	"	"	
Col.4/20	"	"	"	
Col.4/30	"	"	"	
Col.4/40	"	"	"	
Col.5/20	"	"	"	
Col.5/30	"	"	"	
Col.5/40	"	"	"	
IRC.5	6	0		172
Gamma:				
IRC.5/20	"	2	0.15	170
IRC.5/30	"	2	0.08	171
IRC.5/40	"	3	0.80	172
Electron Beam:				
IRC.5/20	"	0		>146
IRC.5/30	"	6	0.10(5),59(1)	
IRC.5/40	"	6	0.10,109(1)	

Note:

* As of 6-7-1990

[Ozone]: 400pphm ;400 mPa.

** Formulations are listed in table 5-9; the number after the slash is the dose in Mrad.

TABLE 5-9

SBR FORMULATIONS PREPARED BY INDUSTRIAL PARTICIPANTS

Nomenclature

Ingredients (pphr)

15 SBR	COPO	N110 Carbon black	aAdditives	Agerite Resin D	Sulfur
Col2[1]	100	45	9.5	1.0	2
Col.1	"	"	"	"	0.1
Col.2	"	"	"	"	0.2
Col.3	"	"	"	"	0.3
Col.4	"	"	"	"	0.4
Col.5	"	"	"	"	0.5
IRC.5[2]	"	"	"	"	0.5

Comments For Tab'e.2:

1.Colonial Rubber Company

2.Industrial Rubber Company

a:

Additives	pphr
Zinc-Oxide	4.0
Stearic Acid	2.0
Antiozonant (Antiozite 2)	3.0
Antioxidant (Agerite White)	0.5
	9.5

5.2 BR AS AN ALTERNATIVE TO SBR:

Work from the previous contract showed that BR with small amounts of syndiotactic 1,2-polybutadiene reduced the required dose for full cure conditions and introduced crystallinity that increased its tensile strength and hot tear strength.

An objective of this study was to determine whether partial curing with sulfur lowers dose requirements without loss of mechanical properties and, at the same time, enhances ozone resistance. A high cis-1,4-polybutadiene formulation of the fully sulfur cured system was prepared (appendix-A); the mechanical properties and ozone resistance data are listed in tables 5-10 and 5-11. Comparison of the results for fully sulfur cured SBR with the data from (1) shows that the mechanical properties of samples prepared in this study are far superior. Hot tear strengths twice the 138 ib/in previously obtained and a 200% modulus 67% higher were observed; the tensile strength is also significantly greater. As observed with fully sulfur cured BR formulations, the samples failed the ozone resistance test. The study then focused on development of radiation crosslinked formulations which require lower doses and yet possess these superior mechanical properties without regard to ozone.

Two partially sulfur cured formulations were developed; one contains 0.5 pphr sulfur and the other . .tains no sulfur. The mechanical properties, formulations, and ozone resistance data are reported in tables 5-12 and 5-13. The formulation which has 0.5 pphr sulfur was tested at 0, 5, and 10 Mrad. It is estimated that an absorbed dose between 5 and 10 Mrad is required to achieve the full cure conditions. At the small dose of 5 Mrad, the hot tear strength was as high as 289±16 ib/in with reasonable mechanical properties; a reduction would make them comparable to those obtained in (1) with 10 Mrad and no sulfur. The partially sulfur cured system also had low ozone resistance. The advantages enjoyed by SBR under similar conditions do not apply to BR. Clearly the nature of the crosslinks and repeating units both play a major role in the ozone resistance of these samples.

Formulations with no sulfur content at zero absorbed dose demonstrated excellent ozone resistance, but this is expected with under cured elastomers. As soon as we increased the absorbed dose to 10 and 15 Mrad, the ozone resistance declined by 50% and 100% respectively. These results confirm a direct link of the crosslink density to the ozone resistance of BR systems. Even though radiation cured BR does not provide the ozone resistance observed in radiation crossliked SBR, it is superior to sulfur cured BR and has the potential to replace SBR as a tank pad compound. Formulations of all BR samples utilized at this study are listed in table 5-14.

TABLE 5-10

MECHANICAL PROPERTIES OF SULFUR CURED BR FORMULATIONS

Formulation Code	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elong. (%)	Hot Tear Strength (lb/in)
27-1	2214±147	1161±84	447±23	282±23
BRS (Su)*	1747±280	780	350	138±32

Note:
* Data reported in the previous Army report (1).

TABLE 5-11

OZONE RESISTANCE TEST FOR FULLY SULFUR CURED BR FORMULATIONS

Formulation Code	No. of Samples	No. of Failures	Ozone Resistance* (Days) Failure	Survival
27-1	6	6	1/24	

Note:

* As of 8-23-90

O_3 Concentration in the chamber is 6 ppm [600 mPa].

TABLE 5-12

MECHANICAL PROPERTIES OF BR
FORMULATIONS FOR PARTIALLY
SULFUR CURED SYSTEMS

Formulation Code*	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
27-3	1347±29	384±13	649±11	211±4
27-3/5	2025±52	779±19	548±5	289±16
27-3/10	2289±86	993±6	508±27	216±16
27-3NS/10	889±42[2]	431±42	410±45[2]	180±7
27-3NS/15	1609±155	624±60	517±82	296±31
27-.1/10**	1280±200	431±12	536±77	235±6
27-.1/15	1753±116	667±25	517±28	275±9

Note:

* Formulations are listed in table 5-14; the number after the slash is the dose in Mrad.

** Formulations contain 0.5 pphr sulfur and 0.1 pphr crosslinking agent (DTUD).

TABLE 5-13

OZONE RESISTANCE FOR PARTIALLY SULFUR BR FORMULATIONS

Formulation Code	No. of Samples	No. of Failures	Ozone Resistance* (Days) Failure	Survival
27-3	6	5	0.04	>21
27-3/5	"	6	0.04	
27-3/10	"	6	0.04	
27-3NS	6	0		>25
27-3NS/10	"	3	0.08	>18
27-3NS/15	"	6	0.04	
27-.1	6	0		>11
27-.1/10	"	6	0.04	
27-.1/15	"	"	0.04	

Note:
* As of 10-8-90
O_3 Concentration of ozone in the chamber is 4 ppm [400 mPa].

TABLE 5-14

BR FORMULATIONS PREPARED USING
THE NEW MIXER AT U.Md.

Nomenclature

Ingredients (pphr)

1254 BR	POLYMER	N110 Carbon black	[a]Additives	Syndiotactic	Sulfur
27-1	125.0	75.0	10.625	0.0	1.5
27-3	"	"	"	4.0	0.5
27-3NS	"	"	"	4.0	0.0

Note:

a:

Additives	pphr
Zinc-Oxide	3.0
Stearic Acid	2.0
Antiozonant (Antiozite 2)	3.0
Antioxidant (Agerite White)	0.5
Antioxidant (Agerite Resin D)	1.0
Santocure	1.125

	10.625

5.3 COMPETITIVE CROSSLINKING AND SCISSION

Samples supplied by industrial participants were incorporated in a study of mechanical properties as a function of ozone exposure. Colonial fully sulfur cured samples were exposed to ozone over periods of 1, 2, and 7 days (Table 5-15). The samples experienced crosslinking process leading to almost doubling of the crosslink density as indicated by increase in 200 % modulus from 1185 to 1946 psi over a period of one day of ozone exposure. Ultimate elongation decreased from 405 to 351 % over the same period of exposure. Exposure times over 1 day did not influence the mechanical properties greatly compared to unexposed sample (table 5-15). Partially sulfur cured IRC samples with zero and 20 Mrad absorbed dose were subjected to the same conditions and their results are presented in table 5-16. Exposure periods of 1, 7, and 30 days of ozone exposure were performed.

In general, mechanical properties remained the same within ±10% of the samples unexposed to ozone. This behavior led us to consider a competitive crosslinking and scissioning reactions occurring simultaneously as samples are exposed to ozone. Alternatively, there may be an anti-ozone protection effect which does not survive sulfur crosslinking but is either created by or is not damaged by radiation curing. The latter mechanism is suggested by the fact that undercured samples of SBR show great ozone resistance. The former mechanism involves such a delicate balance,

TABLE 5-15

MECHANICAL PROPERTIES OF FULLY SULFUR CURED
SBR FORMULATIONS POST OZONE EXPOSURE

Formulation Code	Ozone Exposure (Days)	Tensile Strength (psi)	200% Modulus (psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
Col2	0	3659±221	1185±63	405±23	124±4
Col2	1	3413±367	1946±300	351±40	119±10
Col2	2	3451±141	1883±97	355±12	124±6
Col2	7	3689±196	1883±140	370±30	128±4

NOTE:
Col2 contains 2 pphr sulfur.

TABLE 5-16

MECHANICAL PROPERTIES OF PARTIALLY SULFUR CURED SBR FORMULATION POST OZONE EXPOSURE

Formulation Code*	Ozone Exposure (Days)	Tensile Strength (Psi)	200% Modulus (Psi)	Ultimate Elongation (%)	Hot Tear Strength (lb/in)
IRC.5	0	1462±19	255±20	799±21	121±15
IRC.5	1	1609±21	236±12	828±20	80±11
IRC.5	7	1567±64	243±7	757±31	101±14
IRC.5	30	1889±90	254±11	854±79	156±37
IRC.5/20	0	3368±104	662±43	573±19	198±16
IRC.5/20	1	3169±107	593±11	631±17	198±13
IRC.5/20	7	2885±68	627±20	586±20	238±23
IRC.5/20	30	3327±71	722±21	675±38	198±41

Note:

3 samples per data point were tested.

* Formulations are listed in table 5-9; the number after the slash is the dose in Mrad.

it is difficult to imagine it can maintain that balance over such extended ozone exposures. What is the identity and nature of the protective component or group ?. It appears to be the terminal and pendant vinyl groups. The terminal vinyl is a known protector of polymers exposed to oxygen atoms in space (13). More to the point, total vinyl content has recently been demonstrated to be linked to ozone resistance of butadiene rubber (14). The implication is clear that if this group is related to the extraordinary ozone resistance of SBR, it may be provided without radiation curing and the concept can be extended to ozone protection of other elastomers as well.

It remains to test this notion by Fourier Transform Infrared (FTIR) measurements of vinyl content of various SBR samples. The pertinent data are summarized in table 5-17. The vinyl content of the uncured rubber falls sharply after full sulfur curing but survives partial radiation curing rather well. If so, the crosslinking not only differs in terms of C-C versus S-S but that the latter may yield to greater vinyl depletion.

These results are not definitive. FTIR with the horizontal attenuated total reflectance (ATR) attachement involves difficult technique problems and considerable experimental uncertainty. Nevertheless the results encourage us to use the vinyl model as the working assumption for our future studies of linking phenomenon and ozone resistance. The radiation induced

TABLE 5-17 ABSORBANCE OF C=C VINYL GROUP DOUBLE BONDS AT 910 CM^{-1} FOR RADIATION CURED SBR.

Formulation Code	Dose (Mrad)	Optical Density at 910 cm^{-1}
Radiation cured:		
26-3	0	0.08±0.027
26-3	5	0.06±0.027
26-3	15	0.036±0.018
26-3	20	0.023±0.007
Fully sulfur cured:		
26-1	--	0.015±0.005

crosslinks are of the form C-C rather than bonds introduced by sulfur systems. For radiation introduced crosslinks systems, the mechanical properties including crosslink density remained unchanged, whereas in fully sulfur cured systems, a crosslinking process took place causing overcure conditions. It was observed earlier that over cured systems are more susceptable to ozone attack than cured systems.

Before our work on the vinyl mechanism, we performed an intensive FTIR-ATR study on both fully and partially sulfur cured systems with particular emphasis on unsaturation absorption. Results from the study in terms of the optical density of C=C unsaturation at 965 cm^{-1} versus ozone exposure are plotted in figures 5 and 6. For the case of the fully sulfur cured system a minimal decrease in the optical density was observed over the first hour of exposure. Over the rest periods of ozone exposure the optical density reached a steady level indicating no change of significance. This does not fit the conventional idea that the ozone failure in SBR is caused by the scission of the C=C unsaturation bonds. These findings suggest that the ozone failure is a function of the nature of crosslinks introduced in SBR systems. Once again, the large uncertainties associated with the measurements must qualify any conclusion.

Sulfur-radiation cured systems behaved in a similar manner with a slight increase in the optical density over the first

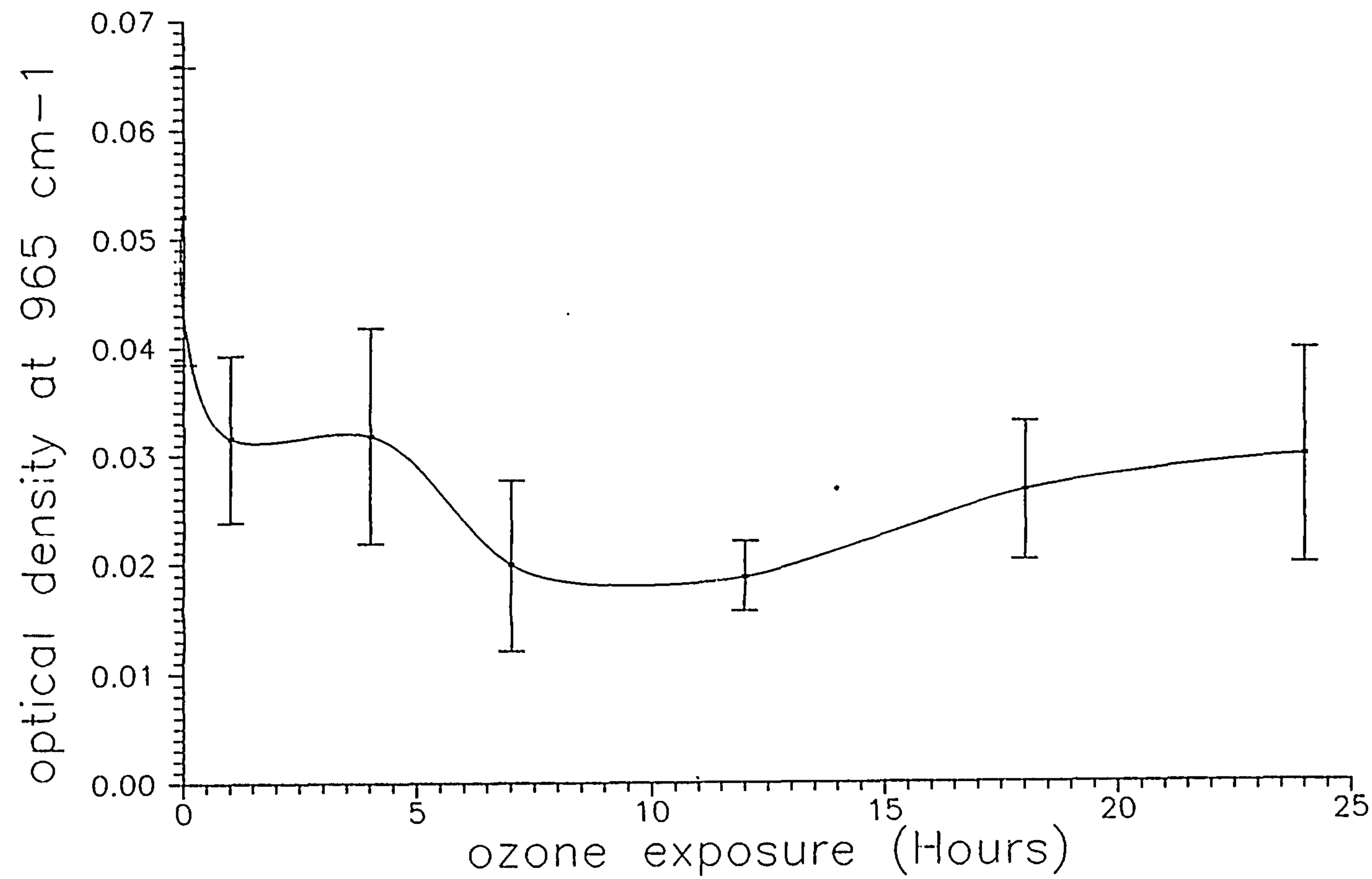


Fig 5. Absorbance of C=C double bonds for fully sulfur cured SBR.

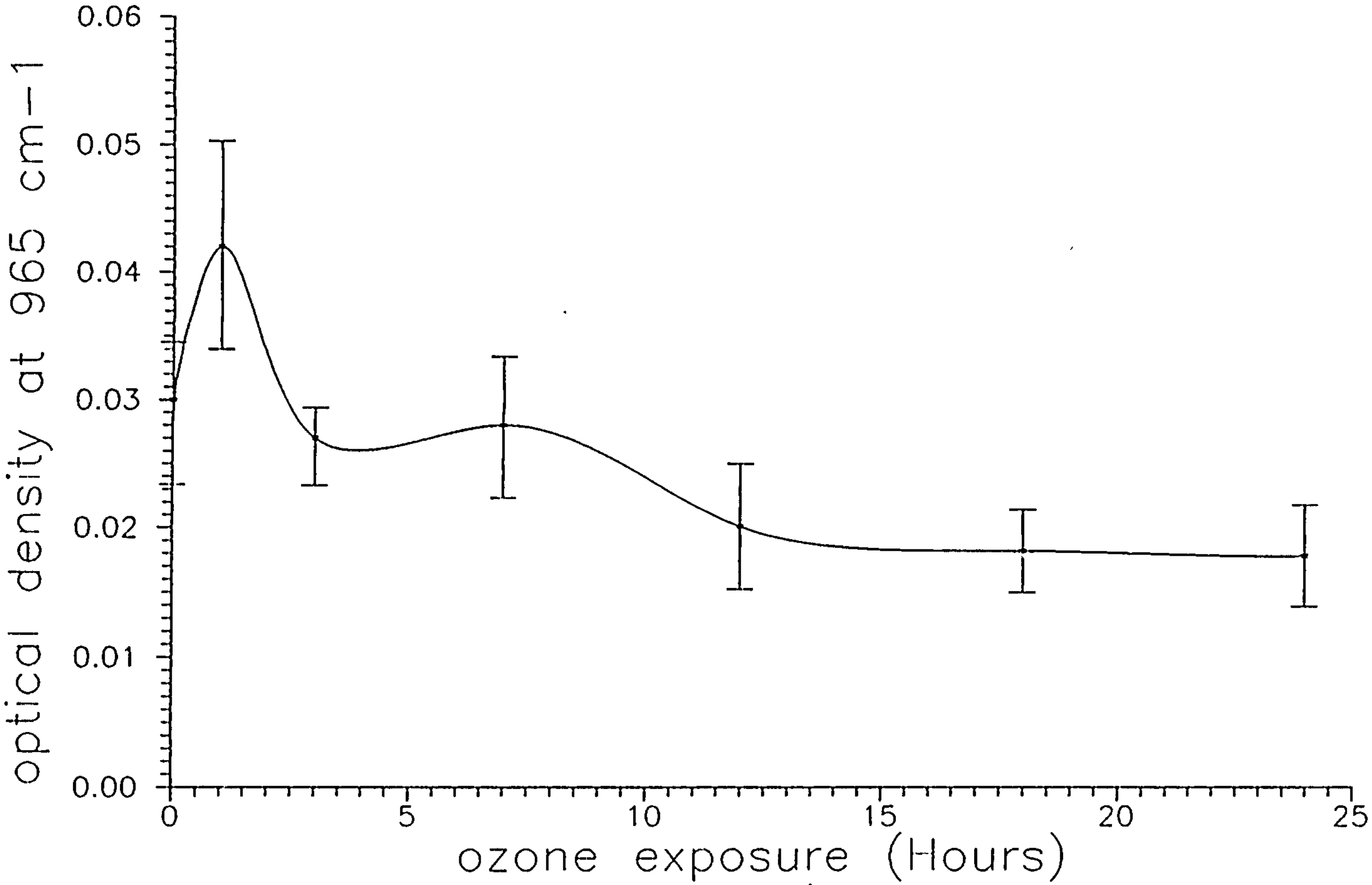


Fig 6. Absorbance of C=C double bonds for partially sulfur cured SBR.

hour of exposure followed by a continuous decrease leading to a steady level over longer periods of exposure. An interesting observation is that both systems reached a comparable steady level of absorbance indicating that the two systems chemical behavior react similarly to long periods of ozone exposure, but behave differently in terms of mechanical failure. This finding coupled with the constant mechanical properties over periods of ozone exposure is consistent with our model that ozone resistance is a strong function of the crosslink density and that the survival of vinyl groups (not the role of vinylene groups) in the radiation linking process holds the key.

5.4 FACTORIAL DESIGN STATISTICAL ANALYSIS

Some of the advantages encountered by using factorial design analysis include; 1. fewer runs per factor studied, and indications of major trends and so determine a promising direction for further experimentation. 2. It is useful when a thorough local exploration is needed, they can be suitably augmented to form composite designs. 3. More detailed, fractional, factorial designs or blocking techniques can be introduced from the preliminary designs so that the degree of complexity of the final achieved designs can match the complexity of the problem. 4. Such designs produce results which can be interpreted by common sense and basic arithmetic. In this study a 2×3 (2^3) factorial design was utilized, where the 2 represents two levels of variations (i.e. minus and plus), and the 3 represents the number of variables selected for the analysis. The two levels were 2.0 - 3.0 pphr of antiozite (An), 0.5 - 1.5 pphr of sulfur (S), and 1.0 - 1.5 of santocure (Sa).

A 2 x 3 factorial design requires eight runs with seven degrees of freedom; 3 main effects, 3 two-factor interaction effects, and 1 three-factor interaction effect. The mechanical properties and the ozone resistance of the various formulations used in the study are reported in tables 5-18,5-20,5-22,5-24,and 5-26. The tables include the coded values of variables which are used in evaluating the effects of their variations and interactions. Interaction effects are established by the multiplication of the variables' respective coded values; for example, An x Sa effect is obtained by the multiplication of the coded values of An by the coded values of Sa. Both main and interaction effects are calculated by the difference between the positive average of response values and the negative average of response values. If the measured response value (i.e. tensile strength) is denoted by Y, then the main effect and interaction effect are determined by:

$$main(interaction)\,effect = \overline{Y}_{+} - \overline{Y}_{-}$$

where $\overline{Y}_{+}$ is the average response for the plus level of the variable and $\overline{Y}_{-}$ is the average response for the minus level. The main effect of a variable measures the average effect of this variable over all conditions of the other variables. On the other hand the interaction effect measures nonadditivity between two variables. Results of both the main and interaction effects are presented in tables 5-19,5-21,5-23,5-25, and 5-27 and plots of the effects in terms of the change in the particular property vs. the levels of concentration are shown in figs. 3 - 8.

The main effect on the tensile strength is still the sulfur, which leads to an increase of 732 psi as we go from radiation-sulfur cured formulations to a fully sulfur cured formulations see table 5-19. Other factors with small but noticeable effect are the santocure and the interaction between antiozite and santocure. Increasing the santocure content tends to increase the tensile strength by 156 psi, while its interaction with the antiozite decreased the tensile strength by 140 psi. The effects of significance were plotted in fig 3 in terms of change in tensile strength as we go from low to high levels of concentration. The response of tensile strength to sulfur and santocure behaved as expected, whereas increasing the antiozite jointly with santocure hindered the tensile strength. Our study of antiozonant chemistry does not disclose the cause.

The sulfur increased the 200% modulus by 382 psi as we go from partially to fully sulfur cured system (table 5-21 and fig 4). An interesting observation was encountered in the case of

TABLE 5-18 DATA FROM 2^3 FACTORIAL DESIGN FOR TENSILE STRENGTH.

Test Condition Number	Antiozite (pphr)	Sulfur (pphr)	Santocure (pphr)	Tensile Strength (psi)
		a. Original values of variables		
1	2.0	0.5/15	1.0	3058±160
2	3.0	0.5/15	1.0	3079±27
3	2.0	1.5	1.0	3638±137
4	3.0	1.5	1.0	3980±49
5	2.0	0.5/15	1.5	3303±330
6	3.0	0.5/15	1.5	3161±170
7	2.0	1.5	1.5	3965±155
8	3.0	1.5	1.5	3949±144
		b. Coded values of variables		
1	-	-	-	
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	

Antiozite (pphr) -	Antiozite (pphr) +	Sulfur (pphr) -	Sulfur (pphr) +	Santocure (pphr) -	Santocure (pphr) +
2.0	3.0	0.5	1.5	1.0	1.5

TABLE 5-19 CALCULATED EFFECTS FOR THE 2^3 FACTORIAL OF THE TENSILE STRENGTH.

Effects	Estimate ± standard error (psi)
Average	3517±409
Main Effects:	
Antiozite (An)	52±69
Sulfur (Radiation curing) (S)	732±69
Santocure (Sa)	156±69
Two Factor Interaction:	
An x S	112±69
An x Sa	-140±69
Sa x S	-32±69
Three Factor Interaction:	
An x S x Sa	-48±69

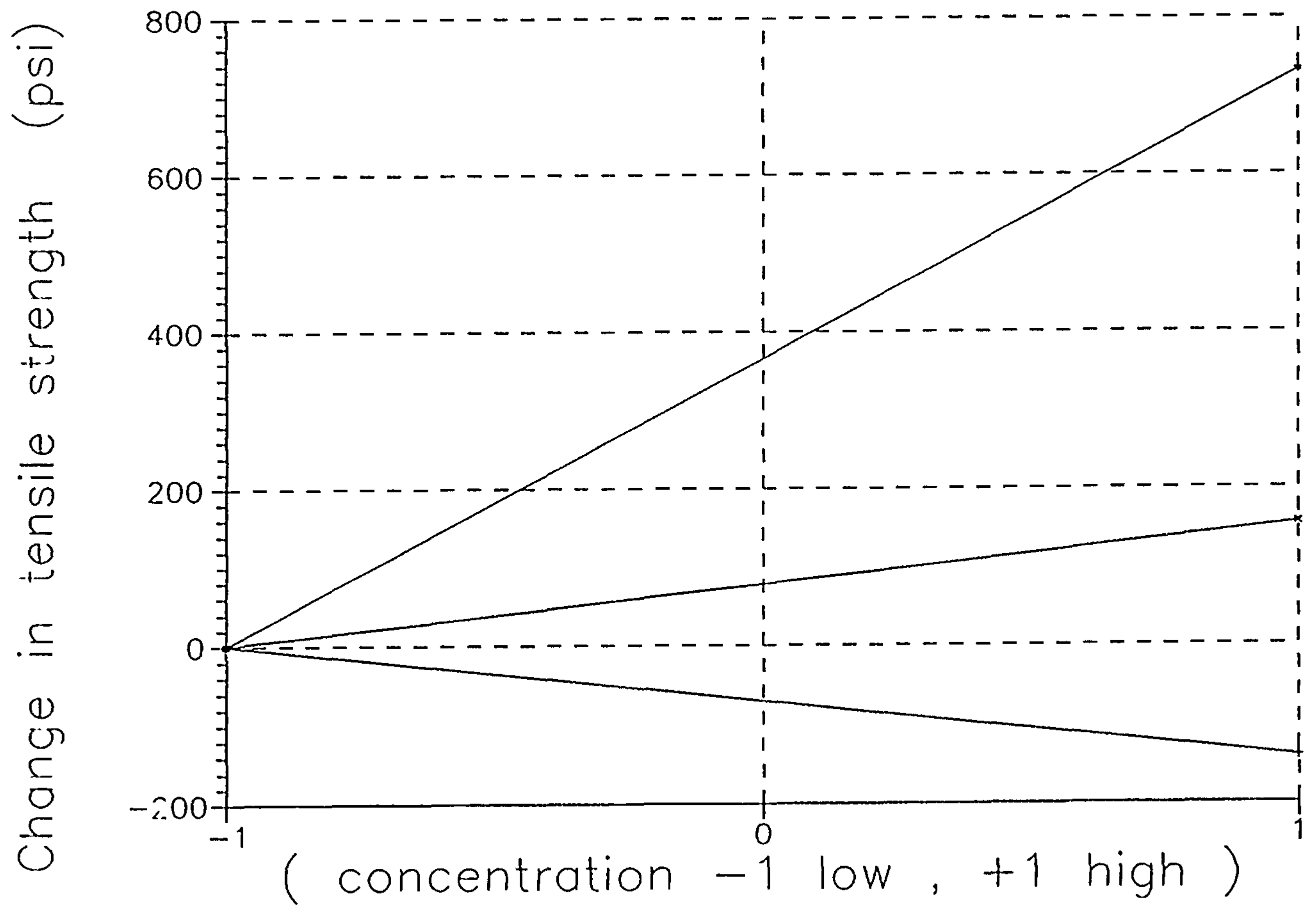


Fig. 7 Main and interaction effects for tensile strength vs. contents levels : (*) effect of sulfur, (x) effect of santocure, (+) effect of An X Sa.

TABLE 5-20 DATA FROM 2^3 FACTORIAL DESIGN FOR 200% MODULUS.

Test Condition Number	Antiozite (pphr)	Sulfur (pphr)	Santocure (pphr)	200% Modulus (psi)
		a. Original values of variables		
1	2.0	0.5/15	1.0	855±29
2	3.0	0.5/15	1.0	745±20
3	2.0	1.5	1.0	1186±33
4	3.0	1.5	1.0	1251±13
5	2.0	0.5/15	1.5	917±10
6	3.0	0.5/15	1.5	691±15
7	2.0	1.5	1.5	1396±8
8	3.0	1.5	1.5	902±42
		b. Coded values of variables		
1	-	-	-	
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	

Antiozite (pphr)		Sulfur (pphr)		Santocure (pphr)	
-	+	-	+	-	+
2.0	3.0	0.5	1.5	1.0	1.5

TABLE 5-21 CALCULATED EFFECTS FOR THE 2^3 FACTORIAL OF THE 200 % MODULUS.

Effects	Estimate ± standard error (psi)
Average	993±254
Main Effects:	
Antiozite (An)	-191±10
Sulfur (Radiation curing) (S)	382±10
Santocure (Sa)	-33±10
Two Factor Interaction:	
An x S	-23±10
An x Sa	-169±10
Sa x S	-37±10
Three Factor Interaction:	
An x S x Sa	-111±10

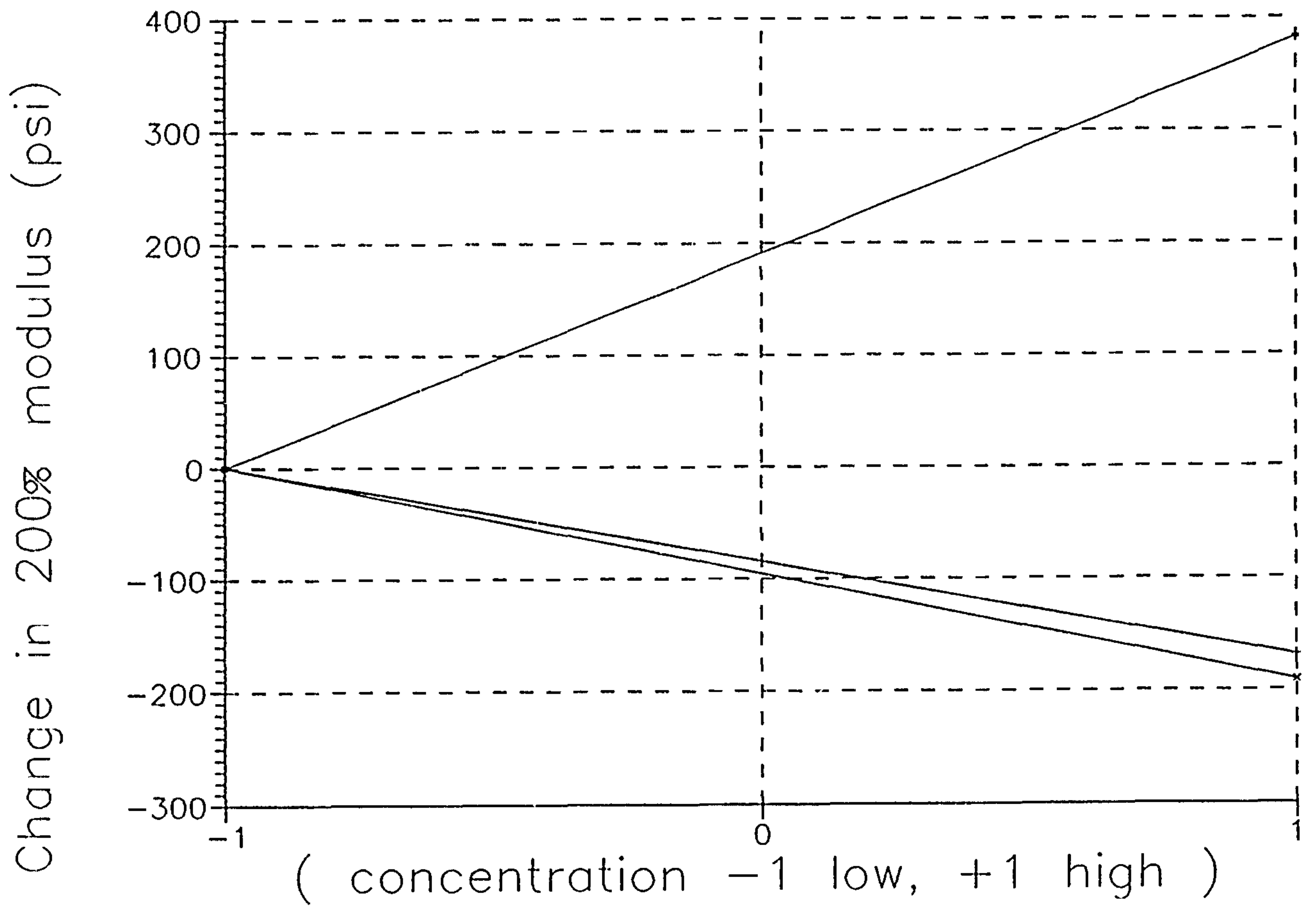


Fig.8 Main and interaction effects for 200% modulus of SBR : (*) effect of sulfur, (x) effect of antiozite, (+) effect Of An X Sa.

the antiozite, where increasing the content by 1.0 pphr led to a decline in the 200% modulus by 191 psi. The presence of the antiozite in SBR systems is necessary in order to improve the ozone resistance, but reduces the crosslink density. This phenomenon may be avoided by radiation crosslinks, where a low concentration of antiozite can be used and good ozone resistance is achieved. Another effect of significance is the two-factor effect of santocure by the antiozite, where a small reduction of 169 psi was observed. Barely significant, this negative effect is mainly due to the antiozite rather than the santocure. Santocure is used as an accelerator of the sulfur crosslinking process. Its presence in SBR formulations can be reduced if ionizing radiation induced crosslinks are the sole source of the curing process.

In the case of the ultimate elongation, a negative difference of 124% was observed due to an increment of 1.0 pphr of sulfur content (table 5-23 and fig 5). A similar behavior of lesser magnitude was encountered with santocure which caused a reduction in the ultimate elongation of 35%. A two-factor interaction of antiozite and santocure surprisingly led to a negative change in the elongation of 49%. Even though most of the effect is influenced by the santocure content, the antiozite seems to magnify this effect by an additional 14% in negative change of the elongation.

TABLE 5-22 DATA FROM 2^3 FACTORIAL DESIGN FOR ULTIMATE ELONGATION.

Test Condition Number	Antiozite (pphr)	Sulfur (pphr)	Santocure (pphr)	Ultimate Elongation (%)
		a. Original values of variables		
1	2.0	0.5/15	1.0	648±50
2	3.0	0.5/15	1.0	702±12
3	2.0	1.5	1.0	578±21
4	3.0	1.5	1.0	551±1
5	2.0	0.5/15	1.5	660±18
6	3.0	0.5/15	1.5	647±17
7	2.0	1.5	1.5	520±20
8	3.0	1.5	1.5	511±9
		b. Coded values of variables		
1	-	-	-	
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	

Antiozite (pphr)		Sulfur (pphr)		Santocure (pphr)	
-	+	-	+	-	+
2.0	3.0	0.5	1.5	1.0	1.5

TABLE 5-23 CALCULATED EFFECTS FOR THE 2^3 FACTORIAL OF THE ULTIMATE ELONGATION.

Effects	Estimate ± standard error (%)
Average	602±73
Main Effects:	
Antiozite (An)	1±9
Sulfur (Radiation curing) (S)	-124±9
Santocure (Sa)	-35±9
Two Factor Interaction:	
An x S	-19±9
An x Sa	-49±9
Sa x S	-12±9
Three Factor Interaction:	
An x S x Sa	21±9

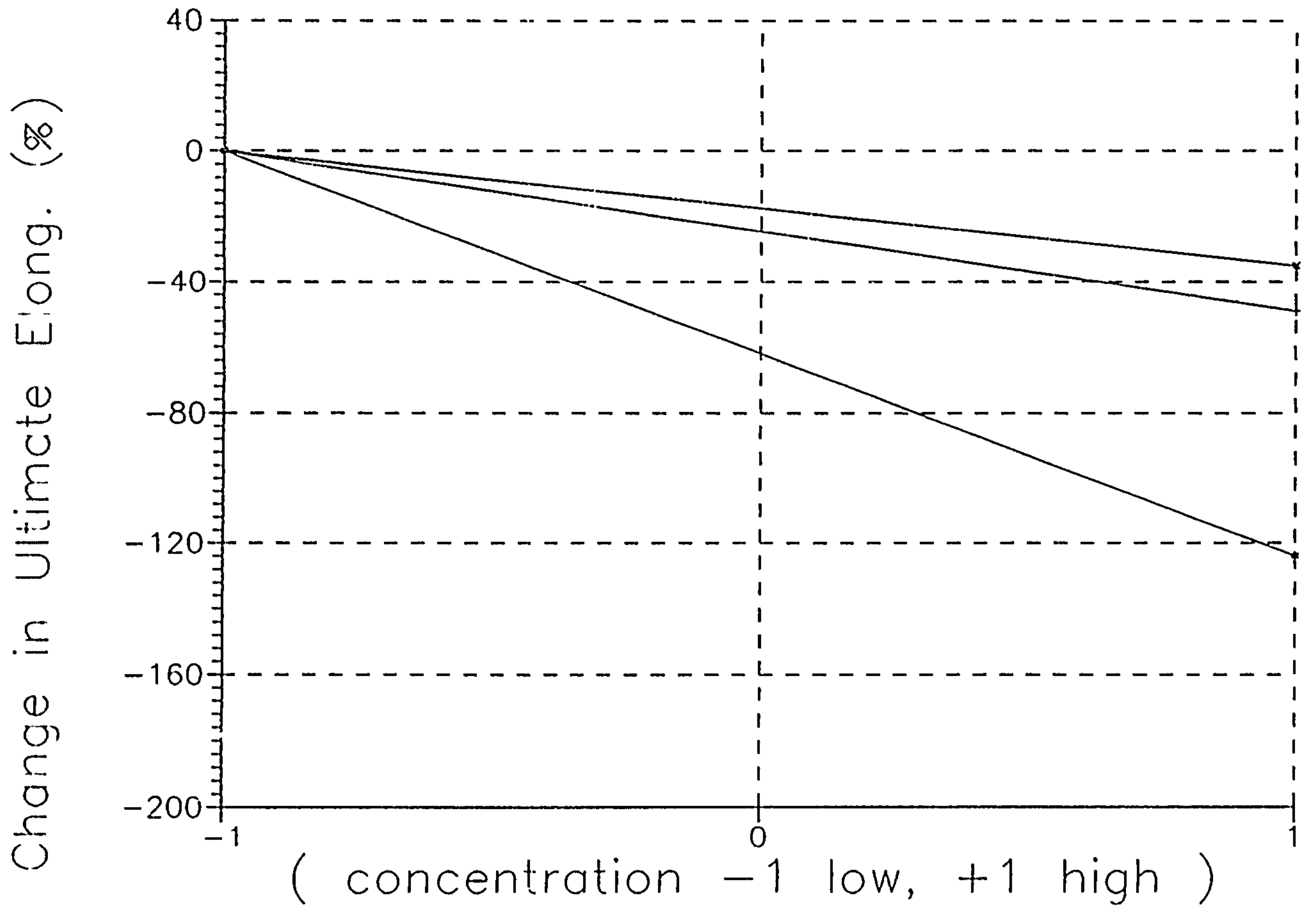


Fig.9 Main and interaction effects for ultimate elong. of SBR : (*) effect of sulfur, (x) effect of santocure, (+) effect Of An X Sa.

TABLE 5-24 DATA FROM 2^3 FACTORIAL DESIGN FOR HOT TEAR STRENGTH.

Test Condition Number	Antiozite (pphr)	Sulfur (pphr)	Santocure (pphr)	Ultimate Strength (lb/in)
		a. Original values of variables		
1	2.0	0.5/15	1.0	209±8
2	3.0	0.5/15	1.0	186±22
3	2.0	1.5	1.0	169±23
4	3.0	1.5	1.0	148±4
5	2.0	0.5/15	1.5	207±18
6	3.0	0.5/15	1.5	204±22
7	2.0	1.5	1.5	143±14
8	3.0	1.5	1.5	147±1
		b. Coded values of variables		
1	-	-	-	
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	

Antiozite (pphr)		Sulfur (pphr)		Santocure (pphr)	
-	+	-	+	-	+
2.0	3.0	0.5	1.5	1.0	1.5

TABLE 5-25 CALCULATED EFFECTS FOR THE 2^3 FACTORIAL OF THE HOT TEAR STRENGTH.

Effects	Estimate ± standard error (lb/in)
Average	177±26
Main Effects:	
Antiozite (An)	-11±7
Sulfur (Radiation curing) (S)	-50±7
Santocure (Sa)	-3±7
Two Factor Interaction:	
An x S	2±7
An x Sa	11±7
Sa x S	-11±7
Three Factor Interaction:	
An x S x Sa	1±7

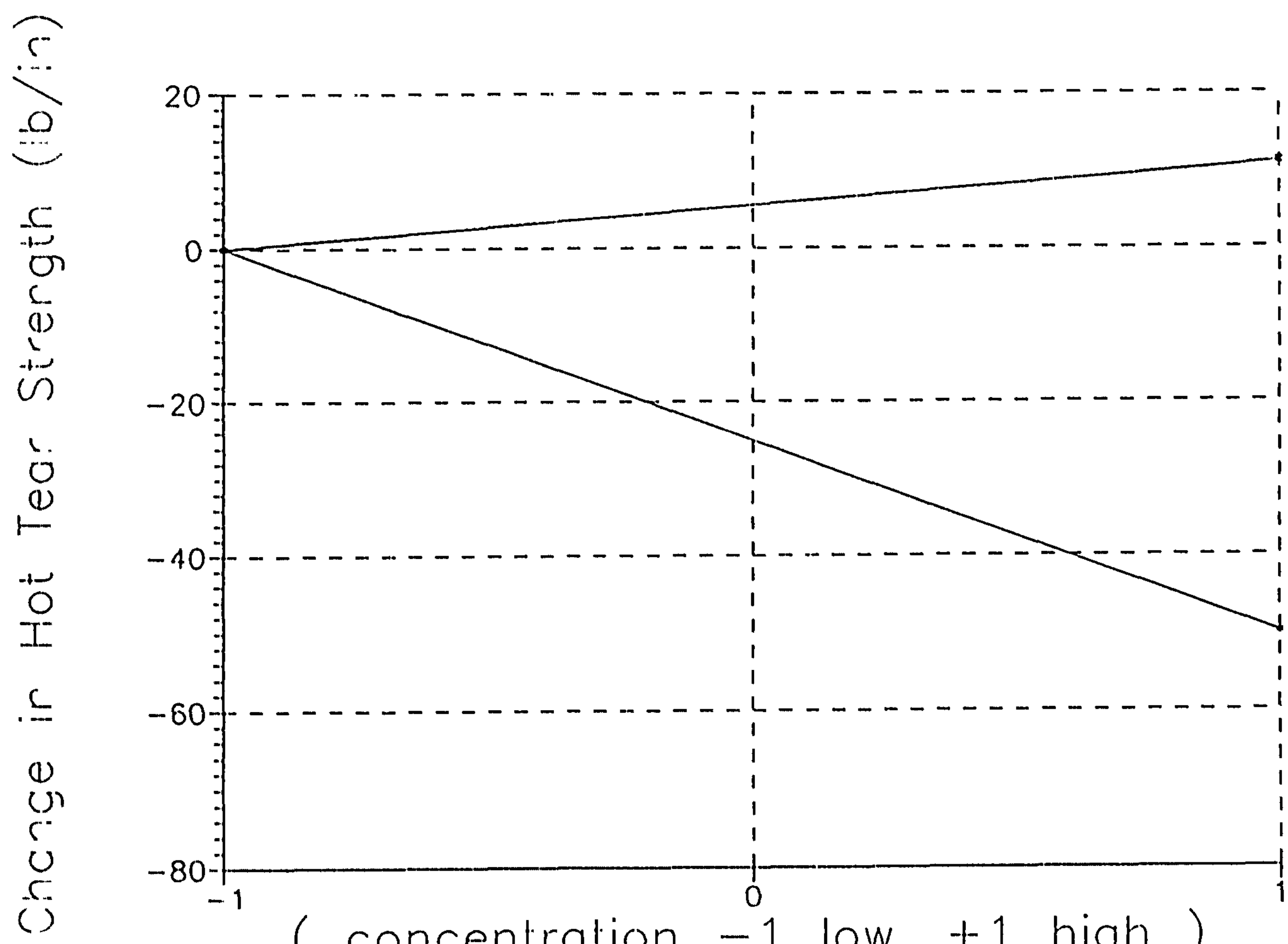


Fig.10 Main and interaction effects for hot tear strength of SBR: (*) effect of sulfur, (x) effect of An X Sa.

The hot tear strength has been the turning point for the effect of sulfur, since the influence of the latter is to decrease the values by 50 ib/in as we go from partially to fully sulfur cured systems (table 5-25 and fig 5). This is the major advantage ionizing radiation cured formulations have over the sulfur cured systems in mechanical properties. As observed earlier, the antiozite lowers the hot tear strength as well as the other mechanical properties. A more detailed investigation of the antiozite effect on the overall performance of the SBR systems is required.

Another point of superiority is demonstrated in the high ozone resistance of ionizing radiation cured formulations over the fully sulfur cured systems (table 5-27 and fig 5). The interesting observation is that as the content of antiozite increased from 2 - 3 pphr, the ozone resistance of fully sulfur cured formulations improved by 15 days. This is not true in the case of partially sulfur cured systems, where the ozone resistance remained the same over the same variation levels. A maximum exposure of 30 days was allowed, even though samples survived much longer under the same exposure conditions.

Our final assessment of the factorial design analysis utilized in this study is that a partially sulfur,

TABLE 5-26 DATA FROM 2^3 FACTORIAL DESIGN FOR OZONE RESISTANCE.

Test Condition Number	Antiozite (pphr)	Sulfur (pphr)	Santocure (pphr)	Ozone* Resistance (Days)
		a. Original values of variables		
1	2.0	0.5/15	1.0	(5/6) 30±12
2	3.0	0.5/15	1.0	(6/6) 30±0
3	2.0	1.5	1.0	(0/6) 0.1±0
4	3.0	1.5	1.0	(6/6) 30±0
5	2.0	0.5/15	1.5	(6/6) 30±0
6	3.0	0.5/15	1.5	(6/6) 30±0
7	2.0	1.5	1.5	(0/6) 0.1±0
8	3.0	1.5	1.5	(4/6) 30±15
		b. Coded values of variables		
1	-	-	-	
2	+	-	-	
3	-	+	-	
4	+	+	-	
5	-	-	+	
6	+	-	+	
7	-	+	+	
8	+	+	+	

Antiozite (pphr)		Sulfur (pphr)		Santocure (pphr)	
-	+	-	+	-	+
2.0	3.0	0.5	1.5	1.0	1.5

Note:

* As of 2-4-91
Maximum ozone exposure allowed is 30 days.
Ozone concentration in chamber is 4 ppm = 400 mPa.

TABLE 5-27 CALCULATED EFFECTS FOR THE 2^3 FACTORIAL DESIGN OF THE OZONE RESISTANCE.

Effects	Estimate ± standard error (Days)
Average	23±13
Main Effects:	
Antiozite (An)	<u>15±3</u>
Sulfur (Radiation curing) (S)	<u>-15±3</u>
Santocure (Sa)	0±3
Two Factor Interaction:	
An x S	<u>15±3</u>
An x Sa	0±3
Sa x S	0±3
Three Factor Interaction:	
An x S x Sa	0±3

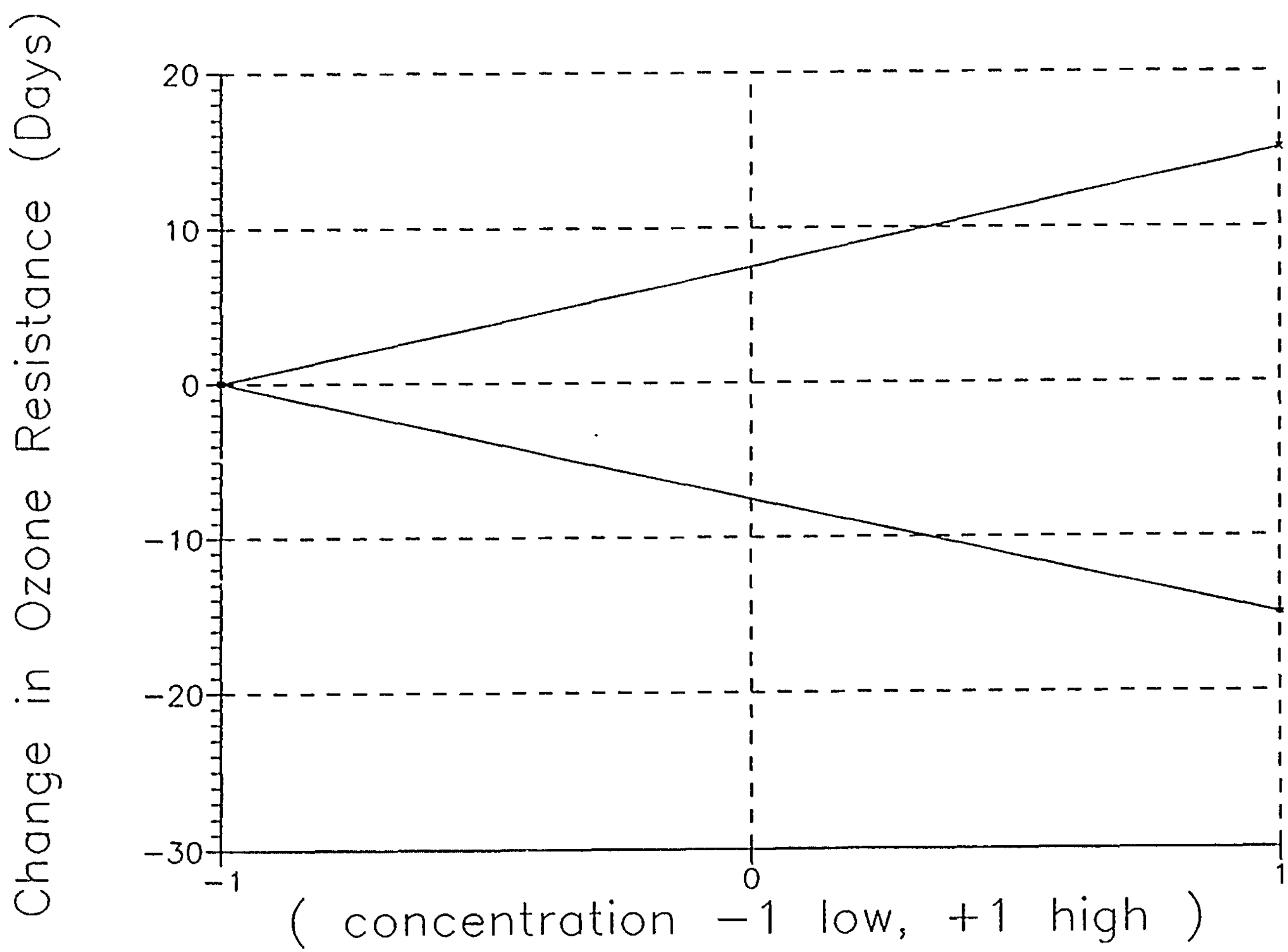


Fig.11 Main and interaction effects for ozone resistance os SBR: (*) effect of sulfur, (x) effect of antiozite.

radiation cured SBR formulation gave optimum cure conditions with a very high ozone resistance. This formulation contains 0.5 pphr sulfur, and cured with an absorbed dose of 15 Mrad, also it contains a low level of antiozite of 2.0 pphr, and a high level of santocure of 1.5 pphr. The mechanical properties and ozone resistance achieved are listed in the following table.

Tensile Strength (psi)	200% M. Modulus (psi)	Ultimate Elong. (%)	Hot Tear Strength (ib/in)	Ozone Resistance (Days)
3303±330	917±10	660±18	207±18	> 30

FUTURE WORK

Future study will try to achieve the following objectives:

(1) A complete investigation of the role of the vinyl group as a protective agent against ozone attack. The study will involve an array of FTIR analysis for various formulations of radiation cured SBR exposed and unexposed to ozone with an emphasis on reducing the uncertainty encountered in the initial study.

(2) Advancing the factorial design program for SBR to establish the optimum concentrations of ingredients to achieve

the most desirable set of mechanical properties and ozone resistance. The focus is on identifying the role of antiozite, higher content of sulfur to reduce dose requirements, santocure, and absorbed dose in the improvement of the mechanical properties and maintaining the good ozone resistance of radiation cured SBR systems.

(3) Establish an understanding of the reason behind the survival of some of the fully sulfur cured SBR formulations after apparently long ozone exposure to ozone. This appeares to be a problem with our ozone chamber.

TABLE 5-28

SBR FORMULATIONS PREPARED USING
U.Md. INTERNAL MIXER FOR THE
FACTORIAL DESIGN STUDY

Nomenclature

Ingredients (pphr)

Test Condition Number	Formulation Code	COPO	N110 Carbon BLack	[a]Additives
1	26-3/15.1	100	45.0	6.5
2	26-3/15.2	"	"	"
3	26-1.1	"	"	"
4	26-1.2	"	"	"
5	26-3/15.3	"	"	"
6	26-3/15	"	"	"
7	26-1.3	"	"	"
8	26-1	"	"	"

Note:

a:

Additives	PPhr
Zinc-Oxide	3.0
Stearic Acid	2.0
Antioxidant (Agerite White)	0.5
Antioxidant (Agerite Resin D)	1.0
	6.5

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ACKNOWLEDGMENT

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APPENDIX A

U.M. STANDARD MIXING PROCEDURES FOR

BR AND SBR SYSTEMS

APPENDIX-A

STANDARD MIXING PROCEDURE FOR SBR AT LRPS

The rubber is mixed in the University of Maryland internal mixer using two approaches as follows:

A. First approach:

1. Heat up the mixer for about half an hour up to 60°C.
2. The mixer has a constant speed of 64 RPM.
3. Charge the mixer with the rubber alone and run it for 1 minute to masticate the rubber.
4. Start mixing by adding the carbon black alone and allow the batch to mix for 3 minutes.
5. Add all the zinc oxide, sulfur, stearic acid, accelerators. antioxidants, and antiozonants which had been previously blended. Allow the batch to mix for 4 minutes before discharging.
6. During the entire mixing the temperatures are not to exceed 104°C.

B. Second approach:

1. Follow the same steps from 1 to 4 as above.
2. Add the previously blended zinc oxide, stearic acid, antioxidants, and antiozonants. Allow the batch to mix for 4 minutes.
3. Discharge the batch and let it cool down to room temperature.
4. Charge the mixer with the batch again and add both the sulfur and the accelerator. Allow to mix for 3 minutes before discharging contents.

APPENDIX-A

MIXING FORMULATION FOR FULLY SULFUR CURED SBR

Ingredient	Concentration (pphr)	Weight (g)
Copo 1500	100.0	150.0
Carbon Black	45.0	68.0
Stearic Acid	2.0	3.0
Zinc Oxide	3.0	6.0
Antiozite	3.0	4.5
Sulfur	1.5	2.25
Santocure	1.5	2.25
Agerite White	0.5	0.75
Agerite Resin D	1.0	1.5

APPENDIX-A

STANDARD MIXING PROCEDURE FOR (BR) AT LRPS

The rubber is mixed in the University of Maryland internal mixer following two stages as follows:

A. First stage:

1. Heat up the mixer for about half an hour up to 150°C.

2. The mixer has a constant speed of 64 RPM.

3. Charge the mixer with the rubber alone and run it for 1 minute to masticate the rubber.

4. Start mixing by adding the carbon black alone and allow the batch to mix for 3 minutes.

5. Add all the zinc oxide, stearic acid antioxidants, and antiozonant which had been previously blended. Allow the batch to mix for three minutes befor dicharging.

6. During the entire mixing the temperatures are not to exceed 170°C.

7. Dicharge the batch and let it cool down to room temperature.

B. Second stage:

1. Adjust the mixer temperature to 40°C.

2. Charge the mixer with the batch and then add the sulfur and the accelerator and allow the batch to mix for three minutes.

3. During this stage the temperatures are not to exceed 110°C

4. Dicharge the batch and then pass it through the roll mill in preparation for vulcanization.

APPENDIX-A

MIXING FORMULATION FOR FULLY SULFUR CURED BUTADIENE RUBBER

Ingredient	Concentration (pphr)	Weight (g)
Budene 1254 (extended oil)	125.0	150.0
Carbon Black	75.0	90.0
Stearic Acid	2.0	2.4
Zinc Oxide	3.0	3.6
Antiozite	3.0	3.6
Sulfur	1.5	1.8
Santocure	1.125	1.35
Agerite White	0.5	0.6
Agerite Resin D	1.0	1.2

APPENDIX-A

Polymer Properties of cold emulsion SBR:

Property	Value (%)	
Styrene Content	23.5	
Butadiene Content	76.5	
Butadiene:		
Cis-1, 4-Butadiene	9.0	
trans-1, 4-Butadiene	54.5	
1, 2-Butadiene (vinyl)	13.0	
Specific gravity	0.94	
Antioxidants & Antiozonants	0.5 pphr	(Phenylene Diamine)

APPENDIX B

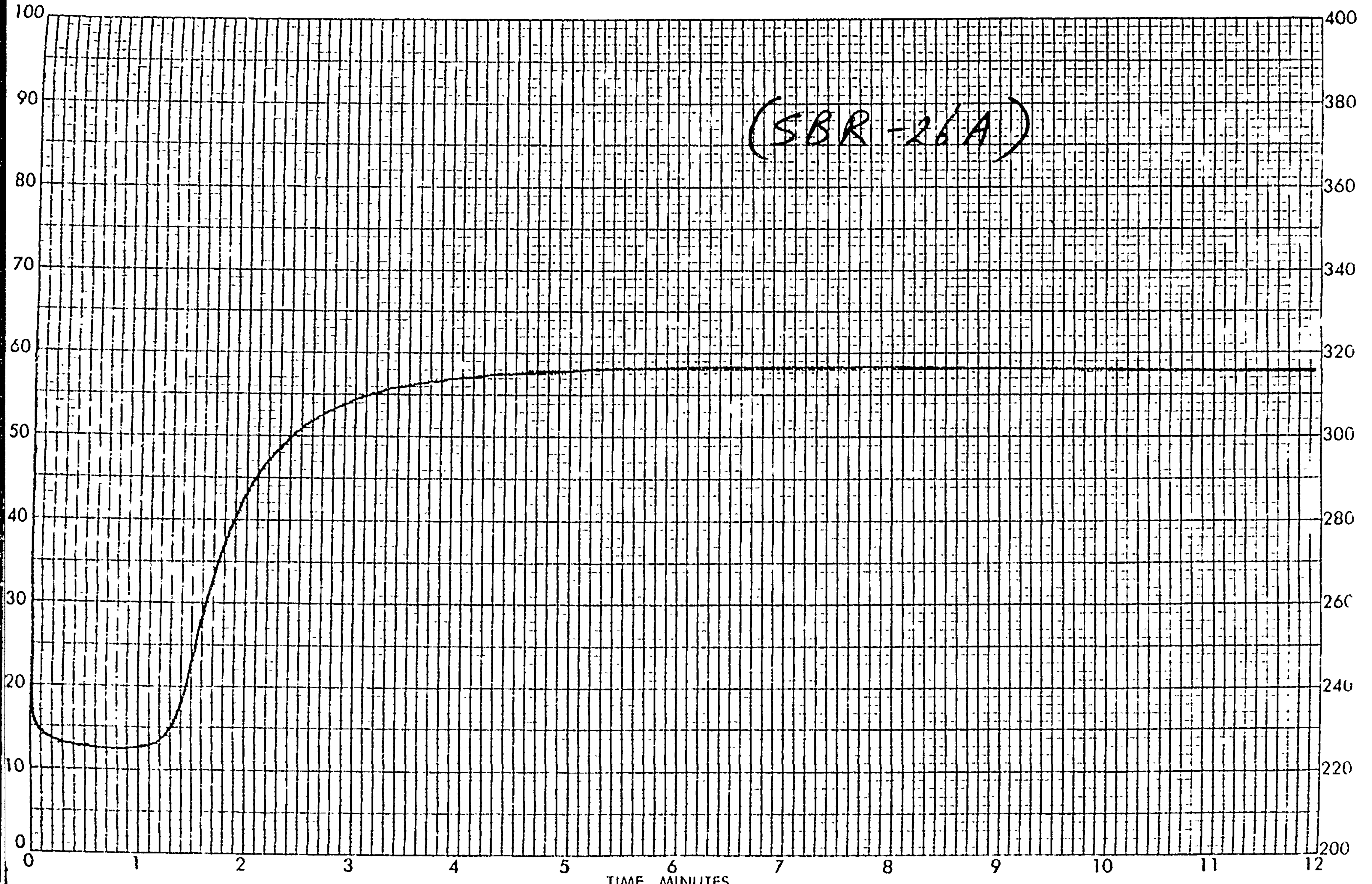
SBR FORMULATIONS RHEOMETER CURVES

Monsanto

LIIJ AC 053

RANGE SET 50 ARC 1 ° DATE ...2-22 1771 OPER. ...

PREHEAT. 0 sec. TEMP: 310 °F PROJ. NO.:

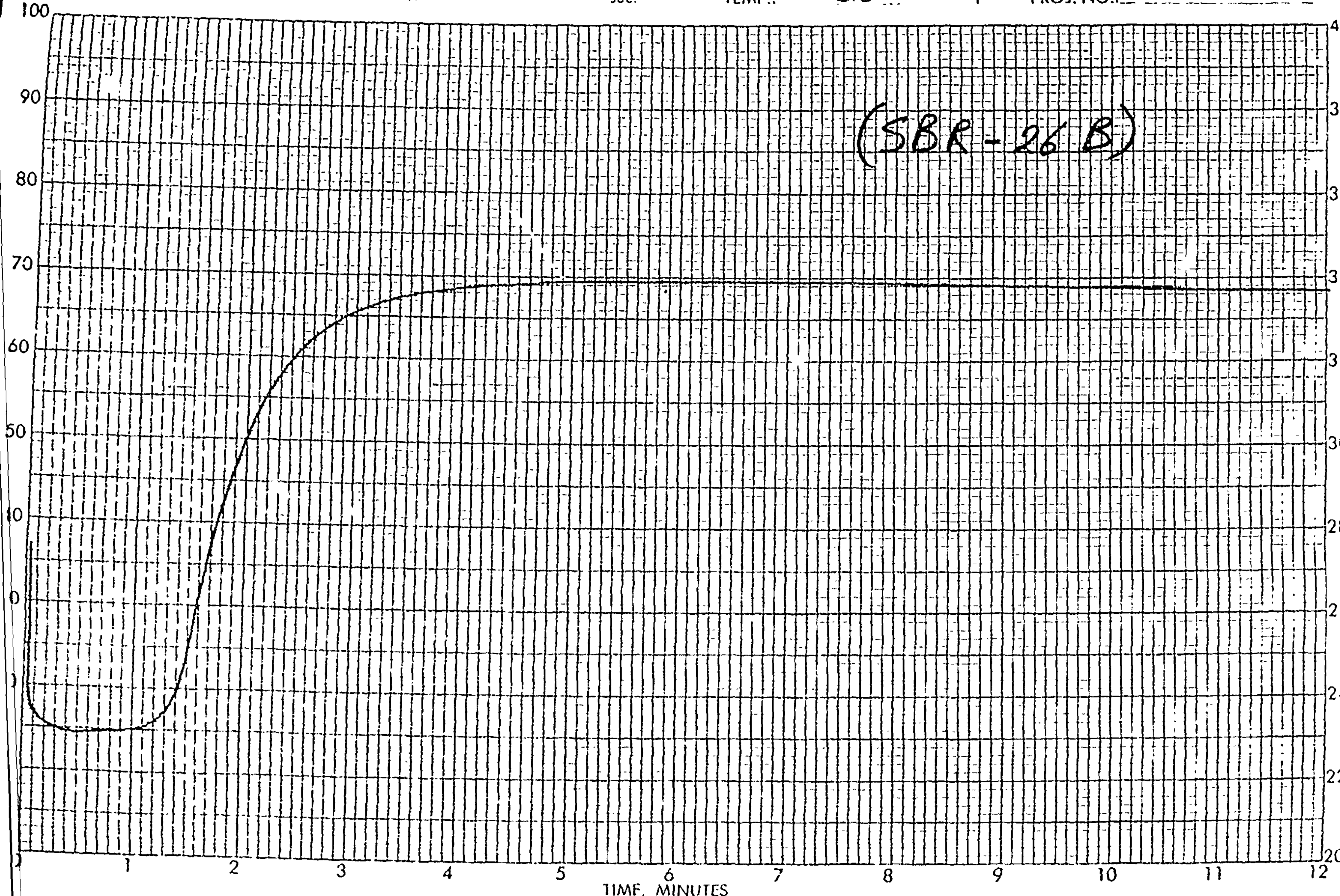


Monsanto.

LID AC 083

RANGE SET 50 ARC 1 OPER.

PREHEAT. 0 sec. TEMP.: 310 °F PROJ. NO.:



Monsanto, AC 053

☑ RHEOMETER ☐ MOONEY

CHART MOTOR ... 24 ... min.

RANGE SEL : 100

PREHEAT: —— sec.

STOCK: [illegible] (4, 5, 6)

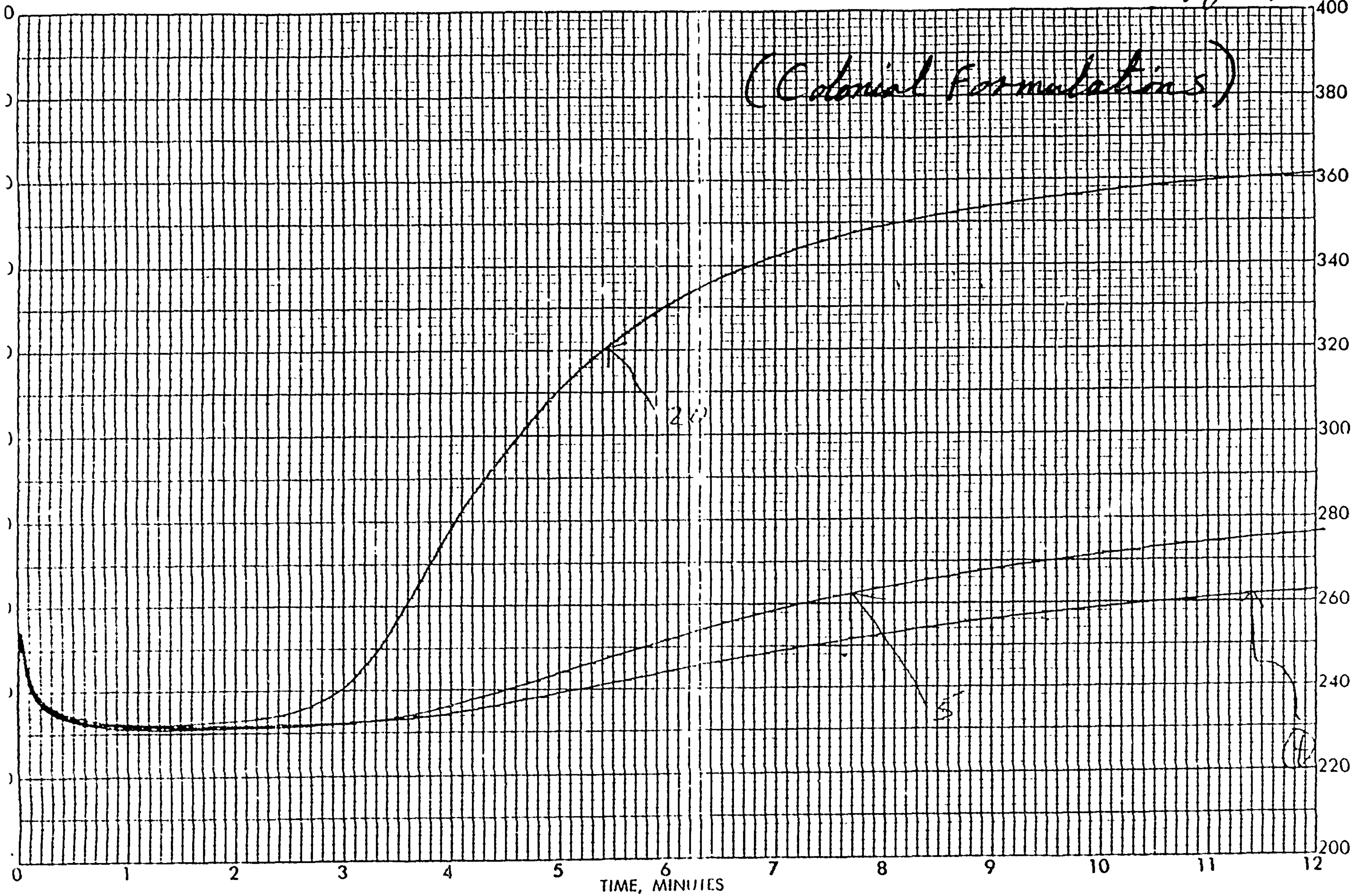
ARC ±: 3 °

TEMP.: 310 °F

DATE: 4/27/87

OPER.: Chris Blalock

PROJ. NO. University of Maryland



(Tests by BRDEC)

T 4160
E 450
M 1190

470
450
440

4320
4210
3960

1180
1210
1140

SBR-26
BRDEC INGREDIENTS

T 3730
E 430
M 1170

420
450
410

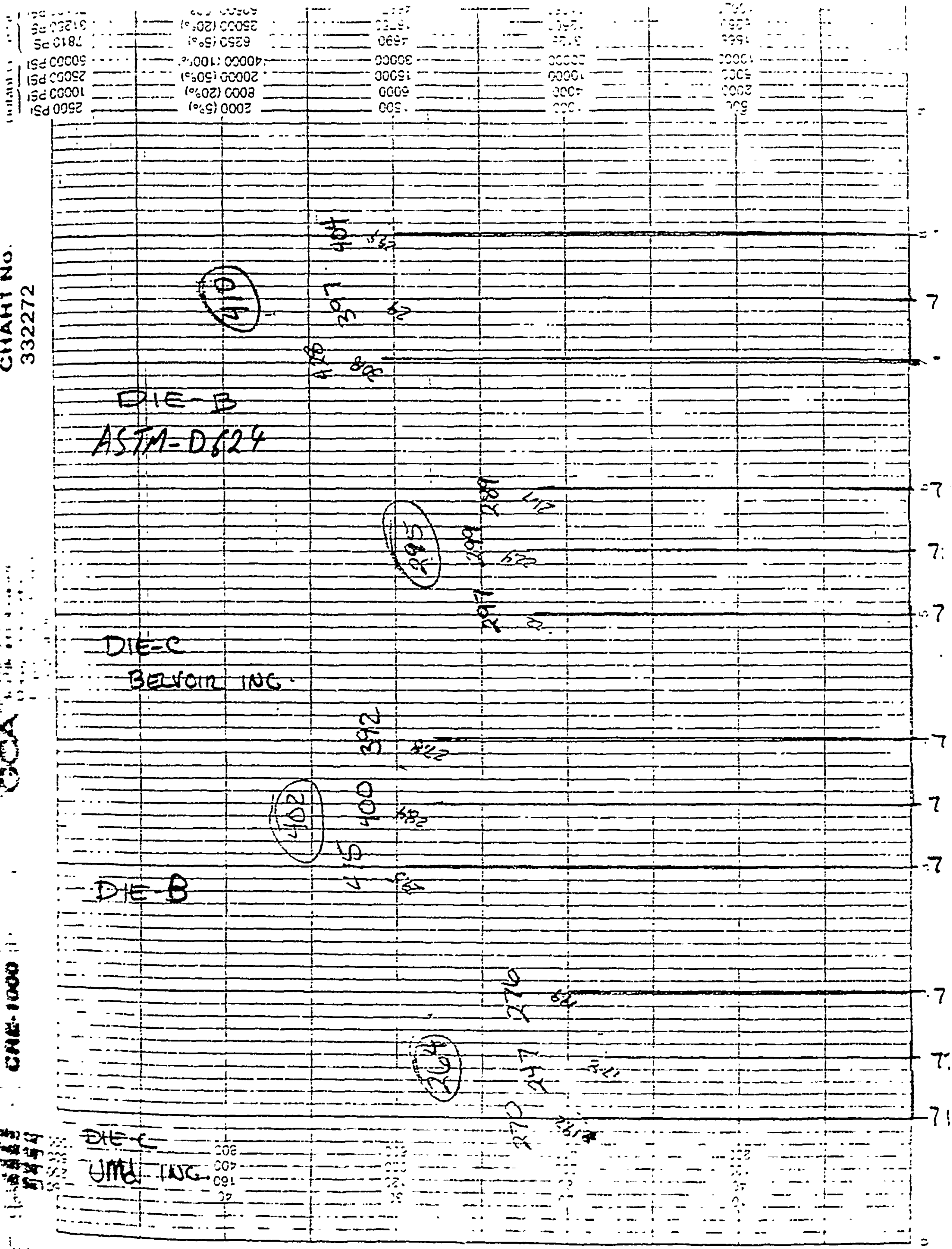
3640
4160
3900

1180
1220
1100

SBR-26
UMd INGREDIENTS

TENSILES

ORIGINAL



TEARS

ORIGINAL

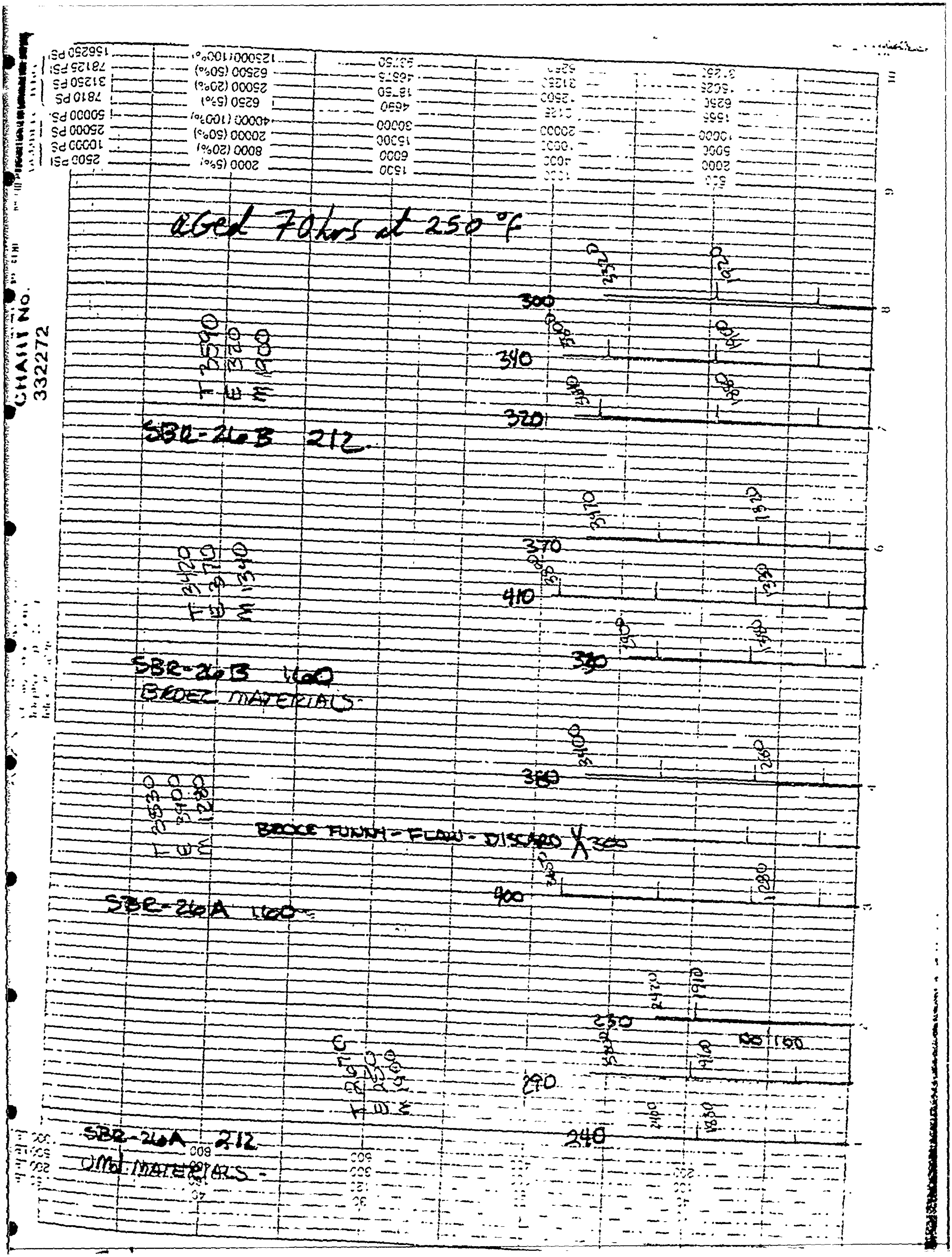


CHART NO.
332272
aGed 70hrs at 250 °F
T 3570
E 320
M 1200
300
340
320
SBR-26B 212
T 3420
E 370
M 1340
370
410
SBR-26B 160
BRDEL MATERIALS
380
BROKE FUNNY - FLAW - DISCARD
400
SBR-26A 160
250
290
240
SBR-26A 212
OMNI MATERIALS

APPENDIX-C

DOCUMENTS OF COOPERATION WITH BRDEC AND NIST

DEPARTMENT OF THE ARMY
US ARMY BELVOIR RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
FORT BELVOIR, VIRGINIA 22060 5606

25 MAR 1987

REPLY TO
ATTENTION OF

Product Assurance Division

Dr. Joseph Silverman
Department of Chemical and Nuclear Engineering
University of Maryland
College Park, MD 20742

Dear Dr. Silverman:

For the past two years, the Chemical and Nuclear Engineering Department of the University of Maryland and the Materials, Fuels, and Lubricants Laboratory of Belvoir Research, Development and Engineering Center have been working together on a program involving the manufacture of rubber. Using the process of radiation curing developed by the University of Maryland and the testing facilities operated by the Belvoir RDE Center, the two organizations have developed a process for curing rubber that endows the rubber with some very remarkable properties.

The need exists for highly ozone resistant and durable rubber for applications such as tracked vehicle track pads, bushings, grommets, hoses, and gas masks. The curing process developed by the University of Maryland has shown to meet these requirements. This process involves irradiating the rubber compounds to induce curing. The normal curing process, vulcanizing, uses sulphur cross-links and heat to cure the rubber. By eliminating the sulphur and the heat the rubber is less susceptible to ozone and wear.

Tests at Belvoir have shown that the hot tear of the rubber has increased by 15-20%. This increase is especially useful in heavy wear situations. Even more amazing is the phenomenal ozone resistance. Vulcanized rubber without ozone resistence compounding normally breaks down after just 5 to 6 days under ozone test. The radiation cured rubber with the same compound has undergone the ozone test for up to 36 days without showing any signs of ozone corrosion. *

The Materials, Fuels and Lubricants Laboratory of Belvoir Research, Development, and Engineering Center commends the University of Maryland, Chemical and Nuclear Engineering Department for its fine work in the area of rubber processing and testing. Their advancements may prove to be a major breakthrough in rubber industry technology.

TROSCOM - PROVIDING SOLDIERS THE DECISIVE EDGE.

Sincerely,

Emil J. York

Emil J. York
Director, Materials, Fuels and
Lubricants Laboratory

* ASTM D-1149 Bent Loop Test - No failures in 36 days when test,

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Gaithersburg, Maryland 20899

May 2, 1988

Professor Joseph Silverman
Department of Chemical & Nuclear Engineering
University of Maryland
College Park, MD 20742

Dear Professor Silverman:

Ozone exposure tests were carried out at the National Bureau of Standards according to ASTM D-1149 (Bent Loop Test) on Army tank track rubber pads vulcanized through high energy electron beam processing. The only deviation from the procedure was that the ozone concentration was about four times that specified in the standard test.

Methods:

Orec Model 0300M Ozone Test Chamber was used for the bent loop test. The concentration of the ozone in the test chamber was measured by the absorption of the ozone in buffered potassium iodide solution and the liberated iodine absorbed by a standard solution of sodium thiosulfate. The test was conducted at 40°C (104°F) at an ozone concentration of about 400 mpa. For cracking detection Heerburgg Microscope Model Wild-M5-40320 was used with magnification of 50x.

High!!

Results:

(1) The conventional cured rubber (15-SBR-24) failed within 3 hours with visible cracks perpendicular on the x-axis of the bent loop.

(2) In the case of SBR of a similar composition (except for sulfur) but vulcanized by irradiation with a high energy electrons beam (absorbed dose 10 Mrad and 15 Mrad), no sign of any cracks was observed after 5 days of exposure to ozone.

Conclusion:

We conclude that vulcanization of SBR-type Army tank track rubber with high energy electrons improves significantly its resistance to ozone attack.

Please call us if we can be of any further assistance.

Sincerely,

Mohamad Al-Sheikhly, Ph.D.
Research Associate
Radiation Interactions and Dosimetry

Robert D. Stiehler, Ph.D.
Polymer Division

The test continued for another month, the electron beam cured rubber did

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